January, 1936

RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
RUBBER DIVISION *of the* AMERICAN CHEMICAL SOCIETY

VOLUME IX NUMBER 1

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Secretary-Treasurer.....C. W. CHRISTENSEN

Vol. IX January, 1936 No. 1

CONTENTS

General Subjects

PAGE

Rubber Division Activities..... v

New Books and Other Publications..... vi

Reprinted Papers

Organic Accelerators and Problems Connected with Their Use in the Factory. By MALDWYN JONES..... 1

Fundamental Studies on the Attributes of Organic Accelerators. XII. Action of Organic Bases on Rubber Sols. By KEIITI SHIMADA..... 15

Studies on the Combined Use of Two Different Organic Accelerators. V. Mercaptobenzothiazole and Hexamethylenetetramine. By ICHIRO AOE and HIROSHI KITAYAMA..... 21

Studies on the Acetone Extraction of Raw Rubber. V. The Influence of Heating at 100° C. and Storage of the Acetone Extract on the Saponification Value. By HIDEMARO ENDÔ..... 35

Self-Vulcanizing Cements. By B. FABRITZIEV, G. BUIKO, and E. PAHOMOVA.. 38

Crystals and Fused Substance in Stretched Rubber (A Preliminary Communication). By PETER A. THIESSEN and WERNER WITTSTADT..... 52

Plasticity and Elasticity, with Special Reference to Unvulcanized Rubber. By J. HOEKSTRA..... 55

Thixotropy and Plasticity in the Rubber Industry. By H. FREUNDLICH..... 64

Entered as second-class matter May 12, 1928, at the Post Office at Easton, Pennsylvania, under the Act of August 24, 1912.

The Oil Resistance of Rubber. I. Study of the Swelling of Vulcanized Rubber. By Yoshio Tanaka, Shû Kambara and Jirô Noto..... 70

Natural and Synthetic Rubber. XV. Oxygen in Rubber. By Thomas Midgley, Jr., A. L. Henne, A. F. Shepard, and Mary W. Renoll..... 74

Rationalization of the Hardness Testing of Rubber. By J. R. Scott..... 83

Porosity in Vulcanized Rubber. By Walter H. Bodger..... 95

The Coating and Impregnation of Textiles with Latex. By H. P. Stevens and W. H. Stevens..... 116

The Natural Stabilizers of Latex. By W. H. Stevens..... 130

Determination of the Color of Latex. By F. H. Cotton..... 132

Note on the Deterioration of Raw Rubber by Manganese Contamination. By J. D. Hastings and E. Rhodes..... 143

Consumers' Crude Rubber Requirements. By George A. Sackett..... 146

Rubber Production. By Edgar Rhodes..... 154

Determination of Total and Free Selenium in Vulcanizates. By E. Cheraskova and L. Veisbrute..... 167

Determination of True Free Sulfur in Vulcanized Rubber. By Syukusaburô Minatoya, Itirô Aoe, and Idumi Nagai..... 172

A Fatigue Cracking Test for Tire Tread Compounds. By E. T. Rainier and R. H. Gerke..... 178

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Easton, Pennsylvania, or The Rubber Service Laboratories Co., Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

Rubber Division Activities

The Rubber Division of the American Chemical Society

Officers

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Sergeant-at-Arms.....L. W. BROCK

Minutes of the Rubber Division Meeting in Akron, Ohio, September 30 and October 1, 1935

The meeting was held in the Ballroom of the Mayflower Hotel, with about four hundred twenty-five in attendance.

The following papers were presented:

1. S. D. Shinkle, A. E. Brooks, and G. H. Cady. AXF—A New Plastic Material.
2. A. A. Somerville. Oxygen Absorbers and Their Effect in Rubber.
3. J. H. Ingmanson and A. R. Kemp. Effect of Different Temperatures and Oxygen Pressures on Rate of Aging of Soft Vulcanized Rubber.
4. B. S. Garvey, Jr. The Chemistry of Soft Rubber Vulcanization.
5. C. Herbert Lindsley. Notes on the Determination of Sulfur in Rubber Compounding.
6. E. W. Oldham, L. M. Baker, and M. W. Craytor. A Rapid and Practical Method for the Determination of Free Sulfur in Rubber.
7. J. H. Dillon. An Impact Cutting Test for Tire Tread Stocks.
8. Bingham J. Humphrey. The Determination of Guanidines in Rubber Stocks and the Consumption of Guanidines during Cure.
9. R. L. Taylor, D. B. Hermann, and A. R. Kemp. Diffusion of Water through Rubber, Synthetic Resin, and Other High Polymeric Materials.
10. S. D. Gehman and H. J. Osterhof. Raman Spectra of Rubber and Some Related Hydrocarbons.
11. Report of Crude Rubber Committee.
12. Business Meeting.

The Rubber Division Banquet was held Monday evening in the Hotel Mayflower Ballroom with about four hundred fifty in attendance. The following committees are to be congratulated for the excellent work which they did in making this Division Meeting a complete success.

General Committee

A. A. Brill
G. L. Allison
A. W. Carpenter
H. I. Cramer

Registration

G. L. Allison
C. B. Moore
W. W. Vogt
H. F. Palmer

Banquet

V. L. Smithers
Enos Baker
J. N. Street
H. P. Protheroe
B. S. Taylor

Trips and Transportation

E. C. Zimmerman
C. W. Sanderson
Grant Duncan
A. B. Merrill

Publicity

C. P. Hall
E. W. Nahm
H. L. Trumbull
N. A. Shepard
L. B. Sebrell

Ladies' Entertainment

Mrs. R. P. Dinsmore
Mrs. N. A. Shepard
Mrs. E. Blaker
Mrs. J. P. Maider
Mrs. H. A. Hoffman
Mrs. G. L. Allison

The Division wishes to thank the following companies for their contributions of fine souvenirs and table favors:

The Rubber Age of New York
E. I. du Pont de Nemours & Co.
R. T. Vanderbilt Co.
Dow Chemical Co.
New Jersey Zinc. Co.
Wishnick-Tumpeer, Inc.
General Atlas Carbon Co.
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American Cyanamid Co.
F. F. Myers Co.
Binney & Smith Co.
Rubber Service Laboratories Co.
Ohio Box Board Co.
Henry L. Scott Co.
Akron Chemical Co.
Anaconda Zinc Oxide Co.
Muehlstein Co.
United Carbon Co.
C. P. Hall Co.
American Zinc Sales Co.
Superior Zinc Co.

Secretary's Report

Total membership to date, Sept. 26, 1935		456
Members paid for 1935	357	
Associate members paid for 1935	99	
New members and Associate members for 1935 (included in above figures)	51	
Total membership not paid for 1935		42
Subscriptions paid for 1935		114
Subscriptions not renewed for 1935	18	
Honorary members and exchanges		30

Treasurer's Report

Balance in bank at the New York Meeting		$4,436.72
Receipts—		
Dues, subscriptions, and back journals	$ 292.00	
Advertising	1,459.93	
Rubber Manufacturers' Association	2,250.00	
Surplus from New York Banquet	174.87	4,176.80
		8,613.52
Expenses—		
Mack Printing Company	2,492.96	
Translations	203.58	
Expenses of N. Y. Meeting	90.82	
Postage, office supplies, telegrams, and telephone	46.65	
Secretarial Service	60.00	
Error in R. C. & T. (American Zinc)	42.50	
Bonds	17.29	
Microphone	73.26	
Printing and Stationery	76.35	3,103.41
Balance in Bank Sept. 26, 1935		$5,510.11

It was voted that the present Secretary and Treasurer be continued for one year.

It was voted that the Secretary be instructed to write a letter of appreciation to President H. E. Simmons for the years of service which he gave to the Division.

The following officers were elected for the coming year:

N. A. Shepard, *Chairman*
H. L. Trumbull, *Vice-Chairman*
L. W. Brock, *Sergeant-at-Arms*
Executive Committee
S. M. Cadwell
O. M. Hayden
W. W. Vogt
A. A. Somerville
A. R. Kemp

C. W. Christensen, *Secretary-Treasurer*

New Books and Other Publications

1934 Report of the Rubber Research Institute of Malaya. Edited by B. J. Eaton. Published by the Institute, Kuala Lumpur, F.M.S. 175 pp.

The annual report of the many divisions of the Rubber Research Institute of Malaya contained in this condensed version reveals that investigations have been conducted from every angle concerning rubber from cultivation to production of finished products. Of particular interest is the report of the Chemical Division, which has spent a good portion of its available time investigating latex properties. This divisional report covers latex components, latex preservation and concentration, and clone latex. Additional investigations are still being carried on by the various divisions of the Institute. [*The Rubber Age*, New York.]

The Rubber Industry—1935. (A Bibliography). Prepared by P. W. Barker. Issued by the Leather and Rubber Division, Department of Commerce, Washington, D. C. 20 pp.

This abridged bibliography is intended for use by the student of the various problems confronting the plantation rubber industry and the rubber manufacturing industry. It has been compiled under seven headings, as follows: The Rubber Plantation Industry; The Rubber Manufacturing Industry; General Information on Rubber; Rubber Restriction and Government Control; Rubber Periodicals; Rubber Publications of the Department of Commerce; and Services on Rubber by the Leather and Rubber division, Bureau of Foreign and Domestic Commerce. Owing to the requirement for brevity, the booklet is not complete in its coverage, but is sufficiently comprehensive to accomplish its purpose. [*The Rubber Age*, New York.]

Rubber Regulation and the Malayan Plantation Industry. Published by the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. 46 pp. 10 cents per copy.

Submitted by American Vice-Consul Harrison Lewis, of Singapore, and revised by E. G. Holt, Assistant Chief, Leather and Rubber Division, this report contains much information with regard to the working of rubber restriction in Malaya that has heretofore been unavailable. It definitely aids American interests in more fully understanding the direction of events under restriction in Malaya up to the present time. The booklet, which is illustrated, thoroughly covers the situation from administration to estimated costs of production. It should make interesting reading for every American rubber manufacturer. [*The Rubber Age*, New York.]

Handbuch der Kautschuk und Asbest-Industrie. Atlas-Verlag G.m.b.H. Berlin-Halensee, Germany, 1935. 251 pp. 15 RM.

A detailed, but concise catalog of German firms engaged in the manufacture of rubber and asbestos goods of all kinds, including soft and hard rubber, balata belting, cables, elastic woven goods, reclaimed rubber, and factice. It also contains alphabetical lists of jobbers, dealers in raw materials, and makers of rubber-like materials, as well as a complete buyers' guide to machinery and technical supplies. An up-to-date catalog of chemical materials used in compounding is likewise given, together with their composition and characteristics.

The list of firms first mentioned is arranged in alphabetical order by cities, and includes relevant data, such as addresses, telephone numbers, products, etc. Other lists are provided with cross-reference numbers. This latest handbook is almost a necessity for those having any contact with the rubber and asbestos industries of Germany.

G. G. HAWLEY

A.S.T.M. Standards on Rubber Products. Prepared by Committee D-11 on rubber products. Methods of Testing and Specifications. October, 1935. Published by the American Society for Testing Materials. 260 South Broad St., Philadelphia. Paper covered. 204 pages. 6 × 9 inches. $1.25 per copy.

This compilation, issued for the first time, affords a convenient laboratory standard test manual. It gives all the twenty-one A.S.T.M. specifications and tests for rubber products, a proposed specification now being considered, and a condensed bibliography.

Included in the compilation are standardized procedures for physical testing, tension testing, adhesion (friction test), hardness, abrasion resistance, chemical analysis, adhesion of rubber to metal, compression set, accelerated aging, and flexing. Also covered by tests are rubber hose (both braided and wrapped) and rubber belting used for power transmission.

Specification requirements, including in most cases definite prescribed tests, are given for a number of rubber products that are extensively used, including cotton rubber-lined fire hose, rubber pump valves, friction tape, rubber insulating tape, rubber gloves, rubber matting, rubber insulating blankets (proposed), insulating wire and cable (3) (Class AO and Class A 30 per cent *Hevea* rubber compound; performance rubber compound).

In the bibliography, sources of information are given concerning properties and testing of rubber. Though the list is not complete, an effort has been made to include references which are comprehensive, and to give the more important of the recent publications. [A.S.T.M. Notice of publication.]

A.S.T.M. Standards on Textile Materials. Prepared by Committee D-13 on Textile Materials. Specifications Tolerances, Methods of Testing, Definitions and Terms. October, 1935. Published by American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. Paper, 246 pages, 6 by 9 inches. Price $1.50.

This compilation of A.S.T.M. standards on textile materials gives all the thirty-seven standard specifications and tests developed by Committee D-13, and in addition provides other data and information in compact form believed important to all who deal with textile materials. The new edition of this book provides new or recently revised standards for the following: woolen or worsted yarns, asbestos yarns and roving, chafer tire fabrics, Holland cloth, hose and belt ducks, light and medium cotton fabrics, pile floor covering, testing fineness of wool, shrinkage in laundering of silk and rayon woven broad goods, strength test of rayon woven fabric when wet, general test methods for cotton fiber. A number of these standards are printed for the first time in the compilation. [*India Rubber World.*]

A.S.T.M. Standards on Electrical Insulating Materials. Prepared by Committee D-9 on Electrical Insulating Materials. Specifications Methods of Testing. September, 1935. Issued Annually. Published by American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. Paper, 311 pages, 6 by 9 inches.

This compilation presents under a single cover A.S.T.M. standards in widespread use for testing and evaluating electrical insulating materials. This edition gives twenty-five standardized methods of test and ten specifications. The method of testing shellac has not been published heretofore. During 1935 revisions were made in a number of the test methods, including those for varnishes, solid filling and treating compounds, molding powders, sheet and plate materials, laminated tubes and round rods, natural mica, and flexible varnished tubing.

Specifications which have been revised cover friction tape, rubber insulating tape, and flexible varnished tubing.

The current report of Committee D-9 outlines the extensive research and standardization work under way and gives a modified Baader saponification test for insulating oils and proposed requirements for rubber insulating blankets.

The following materials are also covered by specifications or tests given in the book: rubber gloves, rubber matting, electrical cotton yarns, silk and cotton tapes, pasted mica, and slate, black bias-cut varnished tape, asbestos yarns, tape, and roving, untreated paper, electrical porcelain, insulating oils. Other tests cover procedures for thickness testing, impact, thermal conductivity, resistivity. [*The Rubber Age*, New York.]

The Chemistry of Synthetic Resins. In Two Volumes. By Carleton Ellis. Published by Reinhold Publishing Corp., 330 West 42nd Street, New York City. 1626 pp. $19.50.

In 1923 Mr. Ellis, widely known industrial research chemist, wrote "Synthetic Resins and Their Plastics." The book reviewed here is intended to replace the earlier work, and was prepared for such purpose because of the large number of synthetic resins and synthetic products which have come to the fore in recent years. The worth of the new volumes may be realized from the fact that almost 15,000 individual patent references are made in the 70 chapters, the index alone containing 206 pages exclusive of the "Trade Names" list of some 1000 items. Space does not permit a résumé of the hundreds of subjects covered. Suffice it, therefore, to state that the minor as well as major developments in the field of synthetic resins have been brought up to date, with their history, development, fabrication, and applications discussed. The subject of modified rubber and synthetic rubber occupies approximately 60 pages, though constant references to the use of resins in the manufacture of various rubber products are made. [*The Rubber Age*, New York.]

Handbook of Industrial Tires. Published by The B. F. Goodrich Company, Akron, Ohio. 24 pp.

Intended for use by operating executives in practically all industries, this booklet tells the story of rubber tires and rubber-tired wheels made by Goodrich for every type of interplant and industrial hauling. One section of the handbook is devoted to reviews of tests proving that rubber tires leave floors unharmed, while steel wheels on industrial equipment cause constant maintenance costs, in addition to other tests favorable to rubber. Another section gives hints on how to select the right tire for the particular type job and how to handle changeovers from steel wheels to rubber-tired equipment. A complete description of the new Goodrich "Vulc-On" rubber-tired industrial wheel is also included. Size and specification tables for many types of industrial tires made by the company round out the handbook. [*The Rubber Age*, New York.]

Brake Linings. The Brake Library, Volume I. First Edition. 1935. T. R. Stenberg, Firestone Park Station, Akron, O. Paper, 91 pages, $8\frac{1}{2}$ by 11 inches. Indexed. Illustrated with 101 figures. Sold by *India Rubber World* at $2 each.

This book is intended to serve as a source of information on brake linings, gathered by research and from experience. The material is arranged to present answers to all questions about brake lining in simple and understandable language.

The topics considered are: Brief History of Braking and Brake Lining, Woven Linings, Impregnating or Binder Materials, Rubber Compounds, Molded Fabric Linings, Molded or Bonded Fiber Linings, Friction Blocks, Testing of Brake Lining, Selection of Linings, and Brake Lining Failures and Troubles.

The brief and concise treatment of every topic covered and the thorough indexing of each combine to make the book a handy and dependable guide for the practical man and machinist interested in the construction and testing of brakes.

Tentative titles for forthcoming volumes in this series follow: "Brake Action and Testing," "Brakes and Brake Drums," "Braking Systems," "Brake Troubles and Correction," "Brake Shop Management," and "Brake Service Merchandising." [*India Rubber World.*]

The Chemicraft Rubber Chemistry Manual. By Jermain D. Porter. The Porter Chemical Co., Hagerstown, Md. 1935. Paper, 76 pages, 5 by 8 inches. Illustrated.

This manual is one of a series written to accompany a student chemical outfit of materials and apparatus for the purpose of instructing the novice in some branch of applied chemistry or microscopy. The story of rubber is covered briefly in seven chapters, which recount Goodyear's discovery of vulcanization, plantation sources of rubber, the chemistry and utilization of rubber, manufacture of tires, wearing apparel, and various other special articles. The final chapter describes the method by which sulfur is procured and refers to a few of its useful compounds. Fifty-two easy experiments are described in detail and serve to impress the student with the utility of rubber to the needs of modern civilization. [*India Rubber World.*]

My World Trip. By E. A. Hauser. Published by Gummi- u. Asbest-Zeitung, Vienna, Austria. English section—26 pp. $1.00. (Available from the Book Department, *The Rubber Age.*)

Consisting of sections in English, German, and French, this book is devoted to the personal observations of the author during his recent world-wide tour. A recognized authority on latex, it is natural that Dr. Hauser was particularly interested in the new uses of latex in manufacturing processes and he records observations in the United States along these lines in footwear, wires and cables, thread, and many special applications. In Japan he was impressed by the modern manufacturing methods in use, and states that they differ from the best installations only in adaptations "necessary to the Japanese manner of living and working." He reports that almost all manufacturing implements required are also "Made in Japan," including moving belts for footwear manufacture, four-roll calenders, large cutting drums, watch-case vulcanizers, and others. Specific reasons for this vast improvement in the production of Japanese rubber goods are extolled. Rubber manufacturing in China at present is in a poor condition, but the author predicts a "seemingly unlimited market" for the future. Impressions of Malaya and Ceylon are included in the book, together with a brief discussion of the working of restriction. For a quick view of the panorama of rubber, "My World Trip" is recommended to all rubber men. [*The Rubber Age*, New York.]

Chemical Engineering Catalog. (Twentieth Annual Edition.) Published by the Reinhold Publishing Corp., 330 West 42nd Street, New York City. 864 pp.

This 1935 edition of the process industries' catalog has more than 100 pages over the previous edition. The separate index of laboratory and reagent chemicals, introduced last year, has been continued. The book section constitutes one of the most complete bibliographies of chemical technology in existence. As usual, the catalog includes classified indexes of equipment, laboratory supplies, heavy and fine chemicals, raw materials used in industries employing chemical processes of manufacture and other subjects. All of the listings have been revised and brought up to date. [*The Rubber Age*, New York.]

Handbook of Chemistry and Physics. Twentieth Edition, 1935. Charles D. Hodgman, Editor-in-Chief. Published by Chemical Rubber Publishing Co., Cleveland, O. Flexible leather binding, 1966 pages, $4^3/_4$ by $6^3/_4$ inches. Price $6.

For twenty-two years the "Handbook of Chemistry and Physics" has been giving a unique service to those in need of accurate tables, formulas, and scientific data in a single convenient volume, and will prove useful to the busy scientist and engineer and acceptable and highly essential in the commercial, educational, and research laboratory. This handbook is now accepted as occupying a field of its own and as being the only authentic guide and reference in the sciences relating to chemistry and physics.

In this edition the organic table has been changed from the tabular style to the paragraph or dictionary style. Instead of having to read across two pages to get complete data on a compound, all the data are in one paragraph, half a page wide. The most important constants, such as melting point, boiling point, and density are indicated by bold face letters so that they can be picked out readily when only this information is wanted. This change in style has resulted in a considerable saving in space, which has enabled the publisher to add data on over 1100 compounds without increasing the total number of pages. The data in the entire table of physical constants of organic compounds have been revised, and the number increased to over 5500. Seventy of the country's leading organic chemists have assisted in checking the constants and in supplying data on important compounds not formerly listed. A formula index of organic compounds has been added. This table is sure to be of great value to those interested in the study and identification of organic compounds.

In the interest of uniformity the twentieth edition contains the general rules and list of words with their recommended pronunciations, as reported by the Committee on Nomenclature, Spelling and Pronunciation of the American Chemical Society.

"Rules for Naming Organic Compounds" is a slightly abridged form of the Definitive Report accepted by the International Union of Chemistry. The table "Prefix Names of Organic Radicals" is in accordance with the latest rules of organic nomenclature. The collection of tables, "Properties of the Amino Acids," had been added, giving in considerable detail the properties of amino acids. Dissociation constants, specific rotation, and solubilities are included. This material will be of particular interest to biological and physiological chemists. X-ray spectra, magneto-optic rotation and colorimetry sections have also been revised to date. [*India Rubber World.*]

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 11, No. 1, pages 37–54, June, 1935.]

Organic Accelerators and Problems Connected with Their Use in the Factory

Maldwyn Jones

A recent article stated that there were about two hundred organic accelerators on the market. Those available differ considerably in type and in price; they vary in general physical properties and in accelerating strength, and in addition they have widely different effects upon the properties of a rubber vulcanizate.

The rubber manufacturer is largely to blame for such a multiplicity of products, but that does not lessen the confusion he feels when called upon to select an accelerator for a particular job. It is evident, therefore, that the problem of selection is one requiring very careful thought and discrimination, and this paper has been designed to give some help in the selection of organic accelerators and to indicate methods of control of their action when applied to specific factory problems.

It has sometimes been argued that the number of organic accelerators is unnecessarily large, and that every effect can be obtained with two or three only. It may be true that the judicious use of, say, three or four accelerators alone or in combination, would give most effects to a reasonable extent, but each organic accelerator imparts to a rubber vulcanizate some property which cannot be obtained to an equal degree with any other product.

The particular factory problems which an accelerator influences may be divided into two groups: (1) production, and (2) quality.

Under these two main headings, questions of milling and processing, of scorching and its avoidance and control, and the problem of flat cure will be discussed, together with methods of compounding to give outstanding aging, superior abrasion, resistance, etc. All these are problems which can largely be influenced and controlled by the correct use of accelerators.

The actual name, accelerator, can be misleading, since it directs attention to one particular aspect of its application, whereas it is important to realize that the function of an accelerator is two-fold. Thus (as the name implies) it enables vulcanization to take place in a shorter time than hitherto, and it improves the physical quality of a vulcanizate in almost every respect. This latter property is probably the more important of the two, and if a tire manufacturer were asked, for instance, why he used mercaptobenzothiazole, it is unlikely that he would reply that it enabled him to vulcanize in 30 minutes but rather that a product with outstanding resistance to abrasion was obtained.

The question of the effect of the organic accelerator upon the quality of the vulcanizate has been dealt with in detail by the author (Jones, *Trans., Inst. Rubber Ind.*, **9**, 337(1934)), and the present paper will deal more with its effect upon factory production and its related problems.

The Classification of Organic Accelerators.—It is possible to group accelerators according to chemical constitution, and the great majority of them fall into five or six chemical groups, such as guanidines, thiazoles, aldehyde amines, thiurams, dithiocarbamates, and xanthates.

Such a classification is of little interest to the practical man, and for him the first and main classification is according to accelerating activity or speed of action,

i. e., according to the extent to which they enable the time of vulcanization to be reduced. No matter what specific properties are required in a vulcanizate, the controlling influence in selecting an accelerator must be speed.

To illustrate the relative speeds of different accelerator types, in a mixture of rubber, 100 parts, zinc oxide, 10, stearic acid, 2, sulfur and accelerator as stated, tensile strength determinations were made.

Diphenylguanidine (DPG)	1.0	Sulfur	3.0
Mercaptobenzothiazole (MBT)	0.625	Sulfur	2.5
Butyraldehyde-aniline (BA)	0.5	Sulfur	2.5
Tetraethylthiuram disulfide (TET)	0.375	Sulfur	2.0
Zinc diethyldithiocarbamate (ZDC)	0.375	Sulfur	2.0

The magnitude and position of each of the curves in Fig. 1 must be taken only as approximate, as the speed of any accelerator can within certain limits be altered by alteration in the proportions of sulfur, or of accelerator, or of the other ingredients. It is believed, however, that the foregoing are typical of the amounts generally used to give optimum results.

Having indicated briefly the usual classification of accelerators, the next problem is the more practical aspect of the control of accelerator action and the problem of scorching. The problem of scorching is a vital one, but provided that adequate precautions are taken it is today comparatively rare. In fact, where scorching does occur today it can usually be traced to failure to observe reasonable precautions or to attempts being made to make an accelerator satisfy conditions entirely beyond its capacity.

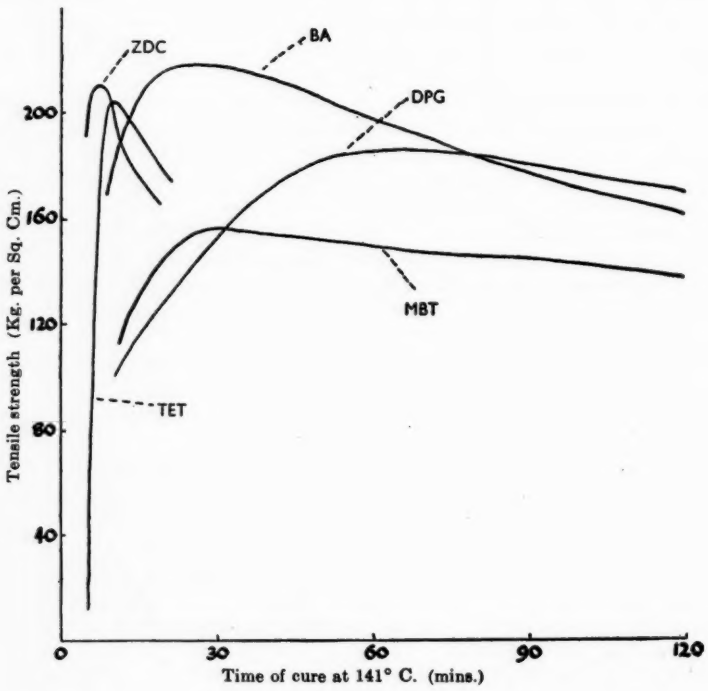

Figure 1

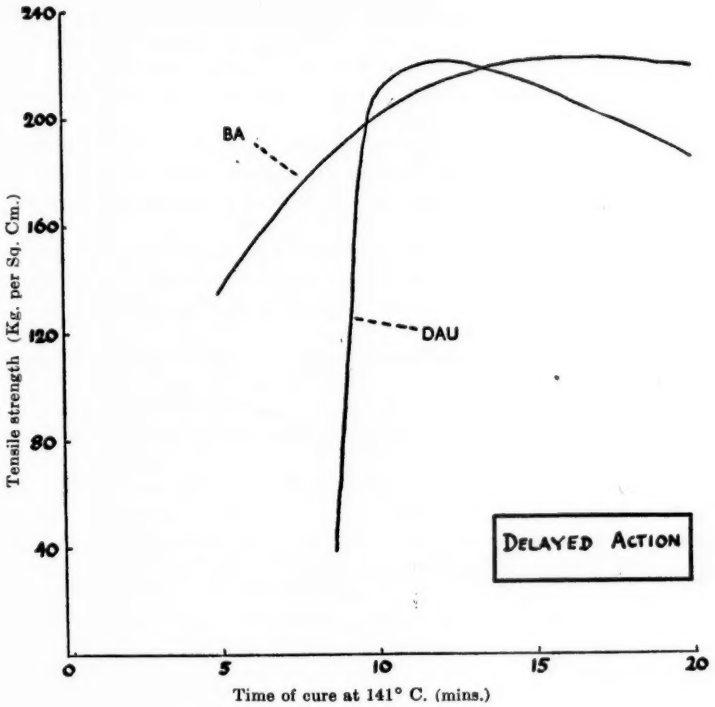

Figure 2

The actual manifestations of scorching or premature vulcanization are well known, but it is an interesting fact that large factories with up-to-date equipment often seem to get more trouble than smaller ones with much inferior outfits, due probably to the very high speed of production in a modern factory. For example, milling and calender bowl speeds are high, and premastication is reduced to a minimum, all factors tending to reduce the margin of safety.

The successful handling of an accelerator may be controlled by a combination of contributory factors which fall under three headings: (1) chemical means, *i. e.*, chemical modification of the accelerator; (2) mechanical means, *i. e.*, processing changes; and (3) physico-chemical means, *i. e.*, suitable compounding.

This paper is not concerned with item (1), but a review of this subject has been made by Naunton, Baird, and Bunbury (*J. Soc. Chem. Ind.*, **53**, 127T (1934)).

Mechanical Means.—Any process change or procedure which leads to a reduction in temperature will help to eliminate scorching. Thus the rubber should be premasticated to as soft a state as subsequent processing will allow.

The mixing-roll temperature should be kept as low as possible. This involves an adequate supply of cooling water and a construction of the system which will allow as rapid as possible interchange of heat between the cooling water and the rubber batch. With this end in view, mills are now constructed with large diameter bore, and the fitting of spray cooling is fairly general. Many plants use specially refrigerated water, and some are now using brine. These considerations become more important as faster mill-roll speeds are adopted. The friction ratio is also an

important factor, the higher the friction ratio the higher the temperature produced. It is usual for mixing operations to have mill rolls approaching even speed.

The size of the nip opening should not exceed a certain maximum; in the neighborhood of $^3/_8$ inch is a convenient opening. Unusually large or small nip openings will tend to give higher temperatures.

The batch should not be run with a large floating bank. The whole of the batch should be constantly and regularly passed through the nip. It is possible to have temperatures in the bank many degrees higher than those registered by the rubber on the roll face.

The mixing procedure should be so arranged that the sulfur and accelerator are kept apart as long as possible. It is usual and preferable to incorporate the accelerator (in master batch form) as early as possible and the sulfur as late as possible in the mixing operation.

On completion of mixing the batch should be quenched in cold water before storage.

The foregoing precautions are of particular importance where internal or Banbury mixing is used, as the temperatures attained are generally in excess of those obtained during open-mill mixing.

Physico-Chemical Means (*Compounding Changes*).—Rubber mixes have to be designed for an ever-increasing number of applications and to meet conditions which are rapidly changing and which are becoming more exacting in their demands. Yet the most noticeable feature between mixes of today and those of ten or fifteen years ago is that those of today are of much simpler composition. The reason for it is probably two-fold, first, the more complete evaluation of the functions which the various fillers fulfil, and secondly, the better appreciation of the properties of organic accelerators.

It is not necessary to deal in detail with compounding practice, but the following points may be enumerated as perhaps the most important to observe if the full value of an accelerator is to be obtained.

Close attention should be paid to the recommendations made with regard to the most suitable amounts of sulfur and accelerator. In general, increase either of sulfur or accelerator leads to greater danger of scorching. Liberal amounts of

Figure 3

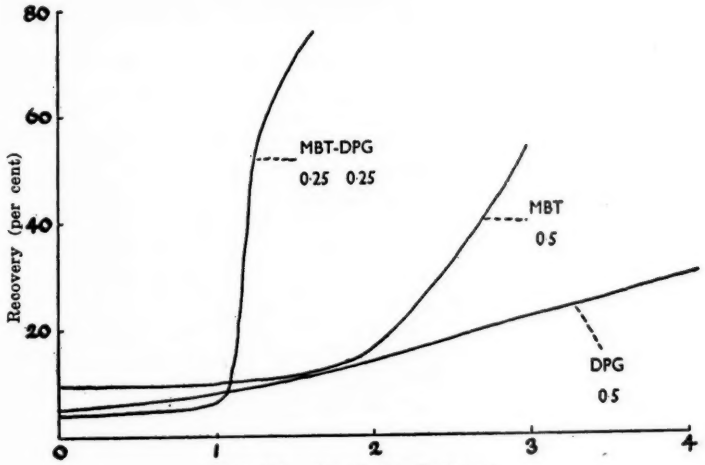

Figure 4

softener help to reduce milling temperatures, and the fact that an accelerator improves almost every physical property of the vulcanizate itself permits adequate softeners to be used without loss of quality.

Vulcanization retarders may be used. These are substances which, when used in small quantities, retard vulcanization at processing temperatures without having any appreciable effect upon its rate at normal curing temperatures. Certain organic acids or synthetic resins have been used to advantage.

The two-batch system can be used, that is, in the case of very fast-curing mixes which have to be stored in between mixing and vulcanization, it is useful to make the batch in two parts, one part containing the accelerator and the other the sulfur. These two portions can then be mixed just before use. This procedure is particularly useful for doughs or solutions. Advantage may also be taken of the properties of mixed accelerators, that is, suitable accelerator combinations may be found which are safe at processing temperatures, yet which are very active at curing temperatures. The extensive use of mixed accelerators has probably been the biggest compounding development in recent years, and it will be dealt with later in the paper.

Methods of Measuring Scorching.—Whereas it is easy to detect a badly scorched batch and also for the experienced factory man to detect the early stages of scorching, some quantitative method of estimating the tendency of particular mixes to scorch is essential in any scientifically controlled factory. Many methods have been described in the literature, but the one used in connection with all the results described in this paper is merely a simple modification of the familiar parallel-plate plastometer. It depends upon the fact that masticated but unvulcanized rubber is essentially plastic and non-elastic, and vulcanized rubber is essentially elastic and non-plastic. Scorched rubber, being in an intermediate stage, has a certain amount of elasticity and plasticity. By measuring the rate of change from the plastic to the elastic state, an evaluation of the degree of scorching can be obtained, and the figure of percentage recovery given in all the graphs is merely an estimation of the extent to which a given sample of rubber will recover after a deforming load is removed. As scorching proceeds the percentage recovery in-

creases, until a fully cured rubber will give (within certain loading limits) 100 per cent recovery.

More rubber is scorched during factory practice than is actually realized. It is possible to work smoothly on a mill rubber which has just set up or commenced to scorch, and it is probable that variation in the service of manufactured articles (particularly composite ones) is frequently due to undetected scorching.

The following experiment will indicate the point in question. A fast-curing mix containing an ultra-accelerator was made in the usual way and stored in the laboratory in a warm atmosphere. Each day the batch was put back on to the mill, run until smooth, removed, and stored. After each milling a sample was taken and tested for scorching in a plastometer. Though on the seventh day the batch ran smoothly on the mill in the usual time, percentage recovery figures showed an increase, indicating that scorching had commenced. Even after the eighth day's milling the batch ran smoothly and no scorching was detected by visual examination, though plasticity determinations showed considerable set-up. Only after the ninth day's milling was difficulty experienced in obtaining a smooth sheet.

These experiments prove the necessity for the choice of a suitable accelerator, as the best results cannot be expected by the use of even a slightly scorched batch of rubber.

Closely connected with the problem of accelerator control and scorching is the problem of delayed action. This is a term which has often been loosely and even wrongly used; for instance, it is often used to describe the properties of accelerators which are safe at processing temperatures, yet which become very active at vulcanizing temperatures. True delayed action is somewhat different, and the expression should be used to denote the lag which some accelerators show at any

Figure 5

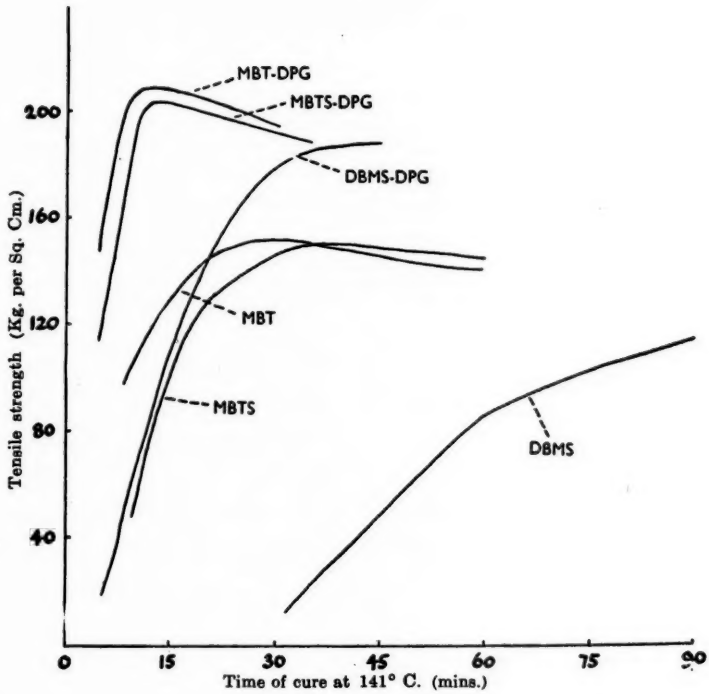

Figure 6

temperature when compared with other accelerators which cure to the optimum in the same time, *i. e.*, it is a time factor and not a temperature factor. The following concrete example will illustrate the point. Figure 2 indicates the tensile strength curves of two mixes compounded with different accelerators and cured at a steam pressure of 40 lbs. per sq. in. (141° C.).

It would be seen that both mixes reached an optimum tensile strength in about 15 minutes. If anything, the mix containing a delayed action ultra-accelerator reached the optimum first. On the other hand, the mix containing butyraldehyde-aniline showed an appreciable cure after 4 minutes, whereas the other mix was entirely uncured. Between 4 and 15 minutes the butyraldehyde-aniline showed a gradual but regular increase in tensile strength. On the other hand the mix containing Vulcafor DAU (the faster one eventually) gave no indication of cure until 7.5 minutes, after which vulcanization set in rapidly. In other words, in the case of butyraldehyde-aniline, vulcanization proceeded steadily from a very early stage in the heating process, whereas in the case of Vulcafor DAU it was delayed for a considerable time.

The property of delayed action has many applications in factory practice, though of course it is in some cases to be avoided. It is useful where thick articles have to be vulcanized, to compensate for the bad heat conductivity of rubber, where multiple presses have to be loaded, to avoid set-up before complete loading, and where articles of complicated shape have to be molded to avoid set-up before complete flow has taken place.

This latter point may be illustrated by the following example. A sheet of rubber

from a fast-curing mix was cured at a steam pressure of 80 lbs. per sq. in.; the sheet of uncured rubber being put in the mold in the usual way and pressure applied. Set-up was so quick, however, that it occurred before the rubber had had time to flow completely into the extremities of the mold. As a result, the rubber was produced in a state of great strain which caused contraction and curling upon removal from the mold. Badly molded articles are often produced as the result of this quick set-up, and a delayed-action accelerator would often remove the difficulty. On the other hand delayed-action accelerators are undesirable in hot air cures or in the open steam or chalk cures of hose or tubing. Here the essential is an accelerator with a quick set-up.

The Control of Accelerator Action by Using Two or More Accelerators in Combination.—The use of mixed accelerators is now a well-established practice. Many proprietary products consist of two accelerators already mixed in some particular proportion, and in a recent paper read before the Institution the use of as many as five accelerators in the same mix was advocated. By the use of a limited number of accelerators, alone and in combination, a wide variety of effects can be obtained. Two accelerators may be used together to produce (1) a greater accelerating activity than either product alone; (2) an accelerating activity intermediate between that of the components; or (3) an accelerating activity less than that of either component. Most accelerator combinations fall within category (1) and a number within category (2), but though instances have been known, it is believed that no combination of marketed accelerators comes within category (3).

The subject will be dealt with in a brief manner, but a few interesting and practical combinations will be illustrated.

The most familiar example is that of combining guanidines and thiazoles, a combination of acidic and basic types giving an activity greater than either alone. Mercaptobenzothiazole is a relatively safe accelerator, but immediately a trace of the slower accelerator diphenylguanidine is added to it, the safety factor disappears and an extremely quick curing mixture is obtained.

The effect produced may be illustrated by reference to the next three figures which show, in Fig. 3, the rate of cure of mercaptobenzothiazole, diphenylguanidine, and

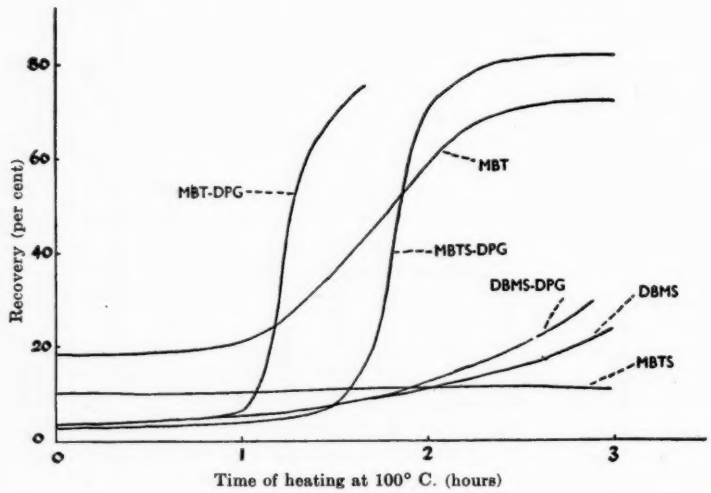

Figure 7

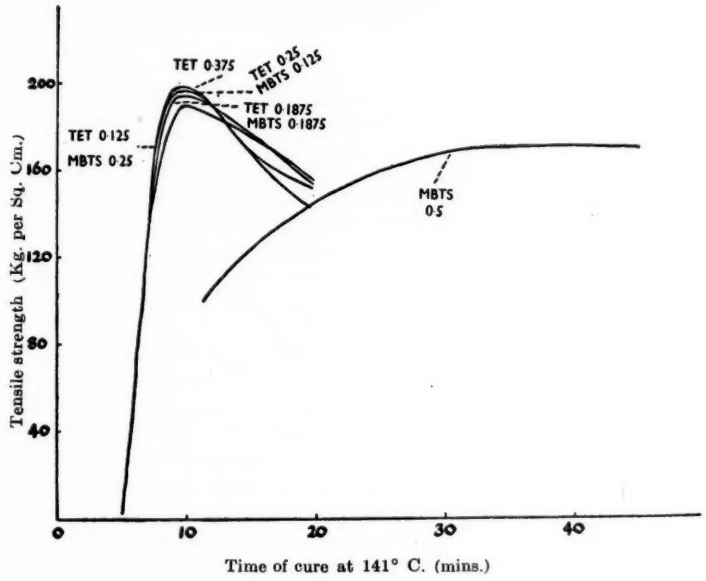

Figure 8

their mixture in equal parts by weight; in Fig. 4, the scorching tendency of such mixtures; and, in Fig. 5, the effect of combining the two accelerators in various proportions. The mix employed in the experiments contained rubber, 100; zinc oxide, 10; barytes, 75; stearic acid, 1; sulfur, 2.5; and accelerator, 0.5 part.

The question arises, where can such combinations be used in practice? Generally speaking they can only be used in relatively thin articles but they are attractive where quick and cheap acceleration is required, where a flat cure is not essential, and where scorching can be controlled. This latter is undoubtedly the greatest limiting factor with combinations of mercaptobenzothiazole and diphenylguanidine. Perhaps the most useful outlet would be in small, molded mechanical goods.

Effects similar to the foregoing can be obtained with greater ease of control by substituting mercaptobenzothiazole (MBT) by dibenzothiazyl disulfide (MBTS) or some other mercaptobenzothiazole derivative. In fact, much of the advance in accelerator practice during recent years has been brought about by modification, chemically or otherwise, of the action of combinations of mercaptobenzothiazole and diphenylguanidine. The variations introduced and the advantages obtained are numerous, but Figs. 6 and 7 serve as a good indication of the main developments. These indicate the effect of mixing diphenylguanidine with (i) mercaptobenzothiazole; (ii) dibenzothiazyl disulfide; or (iii) dibenzothiazyl monosulfide (DBMS).

The examples just cited indicate one convenient method of taking advantage of the unique properties of combinations of mercaptobenzothiazole and diphenylguanidine. The problem can also be attacked by combining a derivative of diphenylguanidine with free mercaptobenzothiazole, and a successful case has been the use of mixtures of mercaptobenzothiazole with acid salts of diphenylguanidine. Such mixtures give absolute safety under all processing conditions, yet give quick set-up at vulcanizing temperatures. They also give higher modulus and stiffer and more snappy products than the thiazoles alone, and altogether represent very

desirable combinations. In fact, such combinations are having very wide application in a variety of rubber manufactures.

Another good illustration of the two-accelerator effect is to be seen in the extensive use of mixtures of thiazoles and thiurams. It should be noted that practically all modern accelerator combinations contain mercaptobenzothiazole in some form or other.

Thiazoles are low modulus accelerators, that is, they generally give soft stocks, but if mixed with thiurams, snappy products can be obtained in quick time and with a surprising degree of freedom from scorching. Such combinations in use today are very numerous, and they are particularly useful for articles such as bathing caps, hot water bottles, molded tubes, and even extruded tubes. Of outstanding interest are mixtures of dibenzothiazyl disulfide (MBTS) and tetraethylthiuram disulfide (TET), as Figs. 8 and 9 will indicate.

A more recent innovation in accelerator combinations is in connection with the popular technic of low sulfur compounding. It is now common practice to use mixes containing very low free sulfur (or even none) and to rely upon the use of high accelerator content giving, by decomposition, sufficient sulfur for vulcanization purposes. Tetramethyl and tetraethylthiuram disulfide are the accelerators usually used. Such mixtures give very flat cures, outstanding aging, and excellent resistance to heat, but as it is necessary to use 2–3 per cent of relatively expensive accelerators, they are often prohibitive in cost. In such cases the judicious admixture of small proportions of a thiazole is both economical and advantageous from the point of view of quality. One illustration will suffice, but a wide variety of cures and of properties can be obtained by making changes in the amount of thiuram, thiazole, and sulfur. This low sulfur technic is undoubtedly very attractive but it has probably been overstressed in some quarters with a resulting reaction, and stability will probably be reached with mixtures of thiurams and thiazoles in combination with about 1 per cent of free sulfur. Such mixtures are free from the defects which the no-sulfur mixes possess.

Figure 10 shows the tensile strengths of mixes compounded as mentioned previously and vulcanized with the stated amounts of accelerator and sulfur.

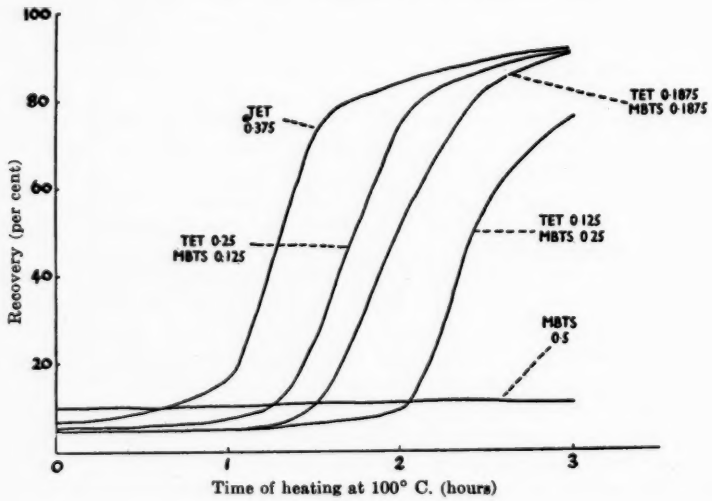

Figure 9

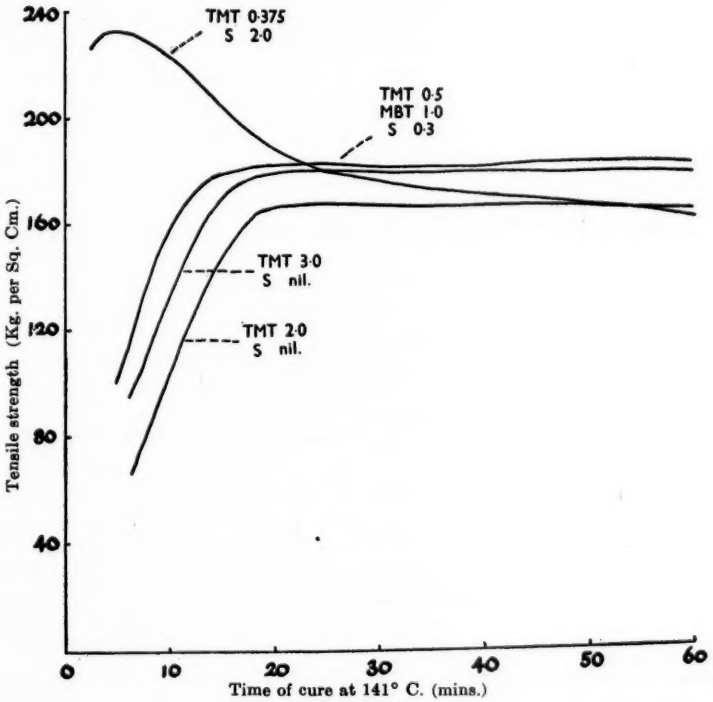

Figure 10

Although this low sulfur technic has been associated chiefly with the thiuram accelerators, it can be applied with equal advantage to several of the slower accelerator types.

The foregoing examples give an indication of the main advantages which may be expected by the use of selected accelerator mixtures. On the other hand the characteristic two-accelerator effect occasionally introduces complications, as for example, in the disposal of factory scrap. This unfortunately cannot be avoided altogether.

It may be produced (*a*) as cured scrap from the spew or trimmings after molding; (*b*) as rubber scorched during some stage of process; (*c*) as uncured but incorrectly compounded stock due to errors in the drug room. The usual method of dealing with such scrap is to mix it in small proportions with satisfactory material and in the case of scrap produced by method (*c*) this is relatively simple. If the scrap is produced either by methods (*a*) or (*b*) it needs to be ground before it can be incorporated into any further mixing even in small proportions, and even then a homogeneous mix is not obtained, but merely a dispersion of cured rubber in uncured stock. The point to observe, however, is to mix the scrap wherever possible into a compound containing the same accelerator. In such cases no material alteration in cure is necessary, but it is easy to visualize what difficulties would be encountered if mercaptobenzothiazole scrap were mixed into diphenylguanidine stock. If admixture of differently accelerated stocks in this way cannot be avoided, then it may be necessary to redetermine curing times. In a factory where only a very limited number of mixes is used, the question of disposal is fairly simple, but in a factory using numerous mixes and accelerators it may be a serious problem.

High Temperature Curing.—A few years ago the vast majority of rubber articles were probably cured in the neighborhood of 141° C. The introduction of ultra-accelerators tended, at least for a time, to introduce lower curing temperatures, particularly as it was advocated that better aging was obtained with lower temperatures of cure. The popularity of low temperature curing has however largely disappeared, and today abnormally high curing temperatures have become almost a fetish, and curing at a steam pressure of 90 lbs. per sq. in. is fairly common practice. Such a practice has many advantages, chiefly advantages concerning speed of production, but it must not be assumed that a mix which is satisfactory at 40 lbs. is also satisfactory at 90 lbs. per sq. in. steam pressure. Apart from other considerations attention must be given to the nature of the accelerator. Some of the thiuram and dithiocarbamate class, for instance, tend to lose efficiency at the very high temperatures, both as regards speed of cure and the best physical quality, whereas mercaptobenzothiazole and diphenylguanidine appear to function quite satisfactorily at the highest temperatures. Some aldehydeamines, particularly butyraldehyde-aniline, seem excellent at high temperatures. Where exceptionally high curing temperatures are to be adopted, it is recommended that the accelerator be kept on the high side.

It is suspected that the necessary time of cure at some elevated temperature is often obtained by applying some rule of equivalent curing times, but such calculations are open to serious errors. Only recently the author read in an article the following statement with reference to equivalent cures. "... Employing the generally accepted empirical rule that intensity of curing action doubles with a rise of 15°F...." and a few days afterwards read another statement that the intensity of curing action doubles with a temperature rise of 13° F. Various other figures have been quoted in the literature, but it is fairly certain that no one conversion figure can be used with accuracy. A series of experiments was carried out to elucidate this point. Using a standard base mixture several compounds were made up, each containing suitable quantities of sulfur and various accelerators. Cures were carried out at a series of temperatures from 125° C. upwards, and from a study of the tensile figures the following conclusions were reached: (1) there is within limits a linear relationship between the time of optimum cure and the temperature of cure, and (2) the magnitude of the relationship is not the same for different types of mixes containing different accelerators. From among six different examples, it was found that the time of cure was halved as the result of an increase in temperature of anything from 12–18° C.; (3) the range over which a linear relationship holds varies with the accelerator; the majority show irregular behavior at temperatures equivalent to a steam pressure of 70 lbs. per sq. in. and over, and with some of the slower types the relationship fails to hold below about 25 lbs. per sq. in.

These points emphasize that where abnormally high temperatures are used, special attention may have to be given both to the nature and the amount of the ingredients used. Also that no general rule can be applied for converting curing times at one temperature to the equivalent cure at some other temperature. Each mix and particularly each accelerator must be tried out separately.

Flat Cure.—The term is used to describe the attainment of a set of conditions such that the physical properties of a mix are maintained over a wide range of curing times. This is an important point as the size, shape, and necessary conditions of manufacture of some articles demand that some portions have a much longer cure than others.

It is, therefore, a desirable requirement to be able to compound the mix in such a way that an overcure of several hundred per cent in any part causes little degradation of the physical quality. Much can be done in this direction by correct com-

pounding, and of the factors influencing the flatness of cure the nature and amount of accelerator is probably the most important. For instance, an overcure of 100 per cent in some mixes would bring about a big reduction in tensile strength, in elongation and in aging resistance, whereas in others high tensile strength may be retained over a range of several 100 per cent overcure, and even the good aging qualities may be substantially retained.

Reference to Fig. 1 will indicate how the different accelerators behave in this respect, but the extremes of peak cure and flat cure may be illustrated by reference to Fig. 10, showing the graphs of tetramethylthiuram as an accelerator both with and without additional sulfur.

The problem of flat cure really centers around the poor heat conductivity of rubber. Heat penetrates thin rubber sheets quickly, and the vulcanization of a thin article (say a bathing cap) may be considered to be carried out essentially at constant temperature; with thick articles, however, a different set of conditions exists, and the curing period may be divided into periods of rising temperature, of approximate constant temperature, and of falling temperature. Under such conditions it is obvious that some portions (usually the outer portion) of a thick article will receive a much greater effective cure than others. The following examples are typical of the cases where flat cure is essential, and the manufacture of a rubber thigh boot is probably as good an illustration as any. This is an article having component parts of different thicknesses; the sole may have a thickness of 1 in. and the top extension a thickness of only $^1/_{16}$ in. To be really successful, such an article must be cured as a unit in a way that the optimum physical properties are attained and not exceeded in every part. The problem may be tackled by giving the article a long, slow rise, and also by a judicious selection of different accelerators for the various sections, but wherever possible it is desirable to have a single accelerator with flat curing properties. Other instances calling for the use of flat curing accelerators are as follows: (1) In the curing of belting in a daylight press. Here, long lengths of belting are cured in sections in such a way that certain portions of the belt have at least a double cure. (2) Where very short cures at high curing temperatures are in operation. In such cases small errors in timing are likely to cause big differences in effective curing times. (3) In the manufacture of composite rubber rollers, where the outer layer is of soft rubber and the inner layer is of hard rubber or vulcanite. In order to have the inside vulcanite layer fully cured, it is necessary to give the whole article a very long cure, and such treatment would result in the outer soft rubber portion having inferior physical properties unless the mix was correctly compounded and particularly unless it had the correct amount of a suitable accelerator. (4) In the curing of tires, particularly large tires. In such cases, although heat may be applied both from the inside and outside of the tire, some portions have very much larger effective cures than others.

In the case of an autoclave-cured giant pneumatic tire with heat applied to the inside (via the air-bag or water-bag) and outside (via the mold), immediately the mold is closed and pressure applied, the outside of the tread and sidewall reaches a temperature very close to the maximum curing temperature, and that temperature is maintained throughout the duration of cure. The sections at the junction of the sidewall and carcass also attain the maximum temperature fairly rapidly, as the heat has only to penetrate through the thickness of the sidewall. In this way different portions of the casing reach the curing temperature after varying times, and the portion of the casing directly under and in contact with the tread probably requires several minutes longer than the outer section of the tread. In this way there are inevitable variations in effective curing times, and the outer sections of the tire receive a considerable degree of overcure. How may the bad effects of this

overcure be minimized? Several methods are available, such as giving the tire a long slow rise, using accelerators of different activity in different parts of the tire, or using the same accelerator throughout but in different proportions. The second alternative is restricted because it is essential to select two accelerators which do not show any substantial two-accelerator effect. For example, to use mercaptobenzothiazole in the tread and diphenylguanidine in the cushion would be a hazardous procedure. The third alternative is the best, as widely differing speeds of cure can be obtained by varying the amount of accelerator and the amount of sulfur. So far the nearest approach to the ideal is probably reached by using mercaptobenzothiazole throughout, but under different conditions, and it should always be remembered that high accelerator and low sulfur tend to give flat cure.

Another important reason for demanding a flat cure is that the different physical properties of a vulcanizate attain their optimum value after varying times of cure. Thus the best resistance to aging or oxidation is probably reached at a curing time somewhat short of that giving the optimum tensile strength. The best resilience is probably obtained at the same curing time as the best tensile properties, but a slightly longer cure is necessary to give the best resistance to abrasion; if the maximum hardness is required then it is necessary to give a cure a long way past the time for the optimum tensile strength. Thus in an endeavor to obtain one physical quality at its best, there is often a danger of others suffering to a marked degree. This applies particularly to resistance to aging, and where bulky articles are to be cured it is necessary to select an accelerator which retains good aging qualities even when cured considerably past the optimum. Of the older types, the thiazoles and certain aldehyde-amines are probably the best, but some of the ultra-accelerators in presence of very low sulfur give astonishing aging results.

Summary.—It may be said that there are three types of problems to be considered when selecting an accelerator:

(1) To determine the approximate limits of curing temperatures and times within which it is desired to work. Questions of skill in handling accelerators and questions of the size and shape of the articles govern this.

(2) To determine what are the specific qualities desired in the vulcanizate, and then to select appropriate accelerators coming within the limits specified in (1) above.

(3) With the choice narrowed down to one or two products, questions purely of an economic nature will probably determine the final choice.

In conclusion the author wishes to express his thanks to the Imperial Chemical Industries Ltd. for permission to publish the results embodied in this paper.

[Translated by K. Kitsuta for Rubber Chemistry and Technology from the Journal of the Society of Rubber Industry of Japan, Vol. 7, pages 212–216, 549–553 (1934).]

Fundamental Studies on the Attributes of Organic Accelerators

XII. Action of Organic Bases on Rubber Sols

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A study of the action of organic bases on rubber sols was made by Whitby and Jane (*Colloid Symposium Monograph*, **1925,** 16), who added small proportions of piperidine, pyridine, diphenylamine, dipropylamine, isobutylamine, benzylamine, etc., to benzene sols of rubber, and determined the changes in viscosity after the mixtures had stood for 10–12 hours. They tried to explain the cause of the lowering of the viscosity brought about by the addition of these chemicals as an electroviscous effect. However, they overlooked an important phenomenon, *i. e.*, the effect of time was not considered in the action of the organic bases. This problem will be discussed later by the author. In the first report, the author pointed out that organic accelerators belonging to the B-type consisted of all amines or their derivatives, the so-called basic accelerators, and that there should be a close relation between the basicity of an organic compound and the extent of its disaggregating effect on rubber. The following experiment was carried out to ascertain the effect of time on the viscosity of rubber sols containing organic bases, a study which may aid in explaining the characteristic properties of B-type accelerators.

1. Method of Experimentation and the Results

Six organic bases, pyridine, piperidine, α-picoline, indole, scatole, and acridine were chosen, and the changes in viscosity with time after the addition of these substances were determined. The rubber samples were prepared by extracting fine pale crepe with acetone for 20 hours, dissolving in benzene, letting stand overnight, separating the insoluble substance by filtration through glass wool, and reprecipitating with acetone, avoiding contact with air and sunlight and drying in a vacuum dessicator containing nitrogen. The method of preparation of the benzene solutions of rubber, the type of viscometer and the method of estimating viscosity, etc., have been described in the first report (*J. Soc. Chem. Ind. Japan*, **35,** 1191 (1933)). The concentration of rubber was 0.45 gram per 100 cc.; the amount of organic base added to 10 cc. of each rubber solution was 0.004 gram. The method of adding these was the same as that in the preceding work.

The viscosity-time relations are shown in Figs. 1 to 3.

Of the six organic bases tested, the addition of pyridine and α-picoline lowered the viscosity of the dilute rubber solutions to a considerable extent in a short time, and the subsequent time had but little effect. This property is in agreement with the author's B-type of accelerator. Though the addition of indole and scatole caused only slight changes in the viscosity, the character of these decreases in viscosity was similar to that of the B-type accelerator. Accordingly, five of the accelerators may be assumed to cause the disaggregation of the rubber in the same way as do B-type accelerators. The effectiveness of these substances in lowering the

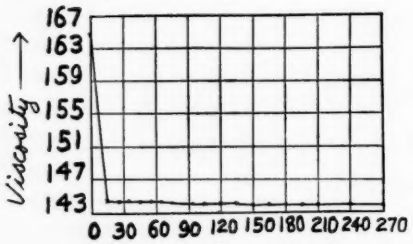

Fig. 1 Piperidine

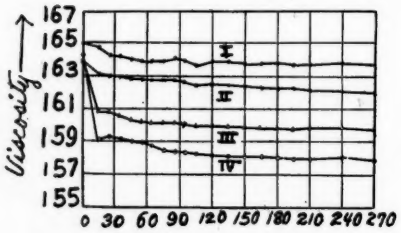

Fig. 2
I. Scatole
II. Indole
III. Pyridine
IV. α-Picoline

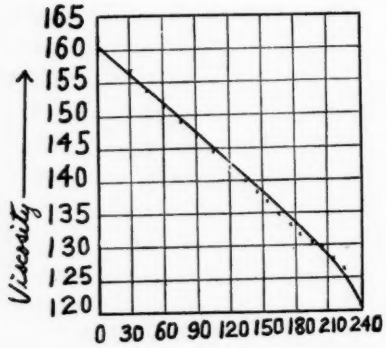

Fig. 3 Acridine

viscosity of the rubber sol was approximately proportional to the strength of their basicity; for instance, a comparison of the dissociation constants of piperidine, 1.6×10^{-3} at 25°, and of pyridine, 2.4×10^{-10} at 15°, and their viscosity-time curves indicates this, and moreover, the fact that weak bases such as indole and scatole have practically no power of lowering the viscosity gives further evidence in support of this view. In other words, these facts indicate that there is a close relationship between the basicity of organic bases and the extent to which they disaggregate rubber; this relationship is also true to a certain extent of B-type accelerators.

The addition of acridine to the rubber sol gave an entirely different result. The curve in Fig. 3 indicates the same tendency as in the case of the author's C-type accelerators. Though acridine is a weak base, it has the property of depolymerizing rubber by increasing the dispersion of the rubber molecules. When the author's equation for estimating the velocity of depolymerization of rubber by heating: $\eta_{t_0} - \eta_t = k\log t$, is applied to the data in Fig. 3, the following values of the constant k are obtained:

Time	$\eta_{t_0}-\eta_t$	k	Time	$\eta_{t_0}-\eta_t$	k	Time	$\eta_{t_0}-\eta_t$	k
15	5.3	4.51	75	13.7	7.31	150	25.6	11.76
25	6.7	4.71	85	15.6	8.09	165	27.8	12.54
35	8.3	5.38	95	16.9	8.54	180	30.0	13.30
45	9.2	5.57	105	18.7	9.25	195	32.4	14.15
55	10.6	6.02	120	20.0	9.62	210	35.4	15.25
65	11.8	6.51	135	23.2	10.89	240	40.2	16.89

These values indicate that the constant k increases with increase in the time t. By plotting the values of t and k, a straight line is obtained. This tendency is the same as in the case of the author's C-type accelerators; accordingly, the rate of decrease in the viscosity of a rubber sol can be expressed by the following equation:

$$\eta_{t_0} - \eta_t = k\log t, \quad k = a + bt$$

By applying the author's theory of the characteristic properties of C-type accelerators (*J. Soc. Chem. Ind. Japan*, **36,** 206 (1933)), the behavior of acridine with rubber sols can be explained in the following way. This substance, though it is an organic base, causes the depolymerization of rubber, and at the same time, it causes a certain chemical reaction; these properties suggest the use of acridine as an organic accelerator (the value of acridine as an organic accelerator will be discussed later). Though it is not clear whether there is a chemical reaction between the rubber molecules and acridine because the products have not been analyzed chemically, the author is much interested in finding a substance among organic bases such as acridine which has the same characteristic properties as have the C-type accelerators, all of which are thought to cause the disaggregation of the rubber. This fact gives strong evidence that the change in viscosity of rubber sols is not caused by an electro-viscous effect, as stated by Whitby.

Summary

1. With the object of ascertaining the effects of organic bases on rubber sols, small proportions of six organic bases, including pyridine, piperidine, α-picoline, indole, scatole, and acridine, respectively, were added to a benzene solution of rubber and the viscosity-time relations were determined. Pyridine, piperidine, and α-picoline changed the viscosity in the same way as did the author's B-type accelerators; indole and scatole also behaved similarly to B-type accelerators, though the change in viscosity was not striking. The lowering of the viscosity by the addition of acridine was on the contrary similar to the effect of C-type accelerators. Based on these results, the conclusion is reached that pyridine, piperidine, α-picoline, indole, and scatole cause a disaggregation of rubber, whereas acridine causes a depolymerization.

2. The rate of lowering of the viscosity of a rubber sol by acridine can be expressed by the equation:

$$\eta_{t_0} - \eta_t = k \log t, \quad k = a + bt$$

It is probable that acridine causes a depolymerization of rubber in the same way as do C-type accelerators, and that it reacts chemically with the depolymerized rubber.

3. An experimental proof is given that there is a close relationship between the basicity of organic bases and their effectiveness in disaggregating rubber.

4. Acridine, which has an action similar to that of C-type accelerators, can be used as an accelerator of vulcanization.

XIII. Action of Organic Acids on Rubber Solutions

As to the action of organic acids on rubber sols, there are the studies of de Vries (*Estate Rubber*, **1920,** 570) and Gorter (*Med. Rubber*, **4,** 35). The former observed a considerable decrease in the viscosity of a one per cent rubber solution in benzene when a trace of acetic acid was added, and the latter found a marked decrease in the viscosity of a rubber sol by the addition of acetic acid or isobutyric acid. Subsequently, Whitby (*Colloid Symposium Monograph*, **1925,** 16) studied the effect of acetic acid, mono-, di- and trichloroacetic acid, benzoic acid, stearic acid, oleic acid, and capric acid on the viscosities of rubber sols, but there is yet no satisfactory explanation with regard to the changes in viscosity of dilute rubber solutions by the addition of organic acids.

In the Twelfth Report of this series, the author discussed the experimental evi-

dence that organic bases, with one exception, bring about the disaggregation of rubber sols; this was of aid in explaining the characteristic properties of B-type accelerators. The object of the experiments described in the present work was to ascertain the effect on rubber sols of organic acids, which have an entirely different

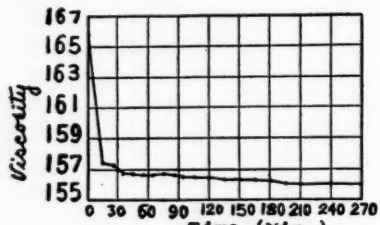

Fig. 1. Butyric acid

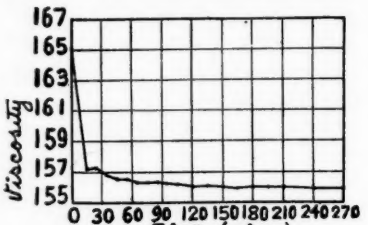

Fig. 2. Valeric acid

ionic behavior from the organic bases, with the hope that the results might be of interest in the colloid chemistry of rubber sols.

Method of Experimentation and the Results

Butyric, valeric, and propionic acids were chosen as representatives of organic acids. Since the effects of acetic and benzoic acid on the viscosity of rubber sol have been reported by Whitby, the author also studied the effect of halogen derivatives such as monochloroacetic acid, bromoacetic acid, *p*-bromobenzoic acid, *o*-iodobenzoic acid, etc., on a benzene solution of rubber, from the point of view that the introduction of a halogen atom to a molecule of these acids might lead to interesting results, since halogens react easily with rubber.

The rubber solution was the same as that used in the preceding experiment; the concentration was 0.45 gram per 100 cc., 10 cc. of which was tested in an Ostwald viscometer, and to which 0.004 gram of organic acid in 1 cc. of benzene was

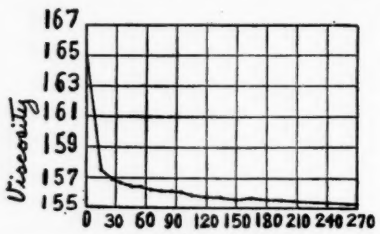

Fig. 3. Propionic acid

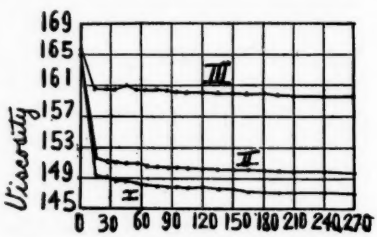

Fig. 4. I. Monochloro acetic acid; II. Bromoacetic acid; III. p-Bromobenzoic acid

added. The effects on the viscosity-time relation of the addition of the organic acids were studied. The conditions, method, and apparatus were the same as described in the Twelfth Report.

The viscosity-time relations are shown in Figs. 1 to 5.

A study of the action of organic acids on the dilute rubber solution from the form of the curves shown in Figs. 1 to 5, indicates that butyric, valeric, and propionic acids lower the viscosity of rubber solutions, progressively with time in the same way as do B-type accelerators and organic bases. That the action of oleic acid on

rubber sols is similar to that of B-type accelerators has been reported already by the author at a meeting of the Nippon Scientific Society on October 29, 1933. It is thus to be supposed that organic acids cause a disaggregation of rubber in the same way as do organic bases.

As to the effect of using halogen derivatives of acetic and benzoic acid, monochloroacetic acid and *p*-bromobenzoic acid cause a sharp drop in viscosity at first, and time has only a slight effect on the viscosity thereafter; this tendency is the same as with B-type accelerators, which cause the disaggregation of rubber. It appears that chlorine or bromine in combination with organic acids has no direct action on rubber. It is of interest to contrast this with the well-known fact that all halogens react chemically with the rubber hydrocarbon (Fisher, *Chem. Rev.* **7**, 83 (1930)).

On the other hand, *o*-iodobenzoic acid depolymerizes rubber, judged by the viscosity-time relation. Accordingly iodine in combination with an organic acid may be said to be very reactive. Application of the data in Table 7 to the author's de-

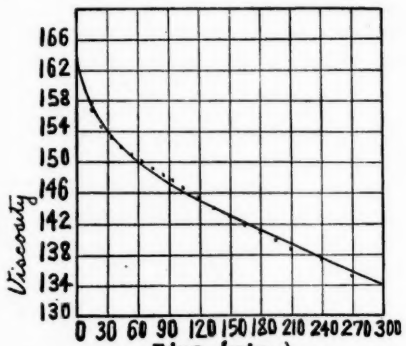

Fig. 5. o-Iodobenzoic acid

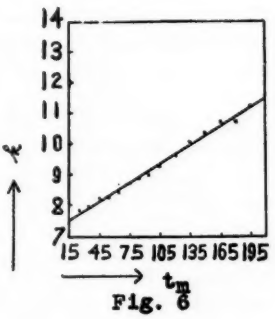

Fig. 6

polymerization formula, $\eta_t^0 - \eta_t = k \log t$, and calculation of k gave the values as indicated in the table below. (η_t^0 is the viscosity of the rubber sol before the addition of reagent, and that of η_t is the viscosity t minutes after such addition.)

o-Iodobenzoic Acid

t_m	$\eta_t - \eta_{t_0}$	k	t_m	$\eta_{t_0} - \eta_t$	k	t_m	$\eta_{t_0} - \eta_t$	k
15	8.8	7.48	75	16.4	8.75	150	22.6	10.39
25	11.0	7.87	85	17.2	8.91	165	23.8	10.74
35	12.4	8.03	95	17.9	9.05	180	24.6	10.91
45	13.6	8.23	105	18.8	9.30	195	25.8	11.27
55	14.5	8.33	120	20.1	9.67	210	26.8	11.54
65	15.4	8.49	135	21.5	10.09	240	28.2	11.85

Figure 6 shows the relation between k and t_m. This relation indicates that *o*-iodobenzoic acid causes a change in viscosity of a rubber sol in the same way as do the author's C-type accelerators (*J. Soc. Chem. Ind. Japan*, **36**, 206 (1933)), and the fact that k increased proportionally to the increase in time t_m may be explained by a depolymerization of the rubber by the *o*-iodobenzoic acid, and its subsequent chemical reaction with the depolymerized rubber.

In short, the author holds the view that organic acids lower the viscosity of rubber sols in the same way as do organic bases, and this effect is attributed to a change in the structure of the micelles which remain in small quantities in the rubber solu-

tion, *i. e.*, a disaggregation. This lowering of the viscosities of dilute rubber solutions by both organic acids and bases in the same way cannot be explained satisfactorily by an electro-viscous effect.

As to the fact that the introduction of a strongly reactive halogen such as iodine into an organic acid, *e. g.*, *o*-iodobenzoic acid, causes the depolymerization of rubber is of further aid in explaining the characteristic properties of the author's C-type accelerators. In most cases, C-type accelerators have the property of causing depolymerization, as they contain a nitro or nitroso group, *e. g.*, in nitrobenzene and dinitrosophenyl dimethylthiocarbamate, and this fact is of interest in the manufacture of C-type accelerators in the future.

Summary

1. To confirm the action of organic acids on rubber sols, small proportions of butyric, valeric, propionic, monochloroacetic, bromoacetic, *p*-bromobenzoic, and *o*-iodobenzoic acids, respectively, were added to dilute solutions of rubber in benzene, and the viscosity-time curves were determined for each case.

2. That organic acids, as in the case of organic bases, cause the disaggregation of rubber was determined from the character of the changes in the viscosity when the acids were added.

3. Among organic acids, only *o*-iodobenzoic acid caused a lowering of the viscosity of a rubber sol, similar to the lowering by the author's C-type accelerators, and the depolymerization of rubber caused by the addition of this acid is due to the presence of iodine in its molecule. Furthermore, the characteristic behavior of C-type accelerators with rubber sols is attributable to the presence of such reactive groups in the molecule.

[Translated by K. Kitsuta for Rubber Chemistry and Technology from the Journal of the Society of Rubber Industry of Japan, Vol. 7, pages 482–504, August, 1934.]

Studies on the Combined Use of Two Different Organic Accelerators

V. Mercaptobenzothiazole and Hexamethylenetetramine

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I. Introduction

Hexamethylenetetramine alone is a very poor accelerator, but in combination with other accelerators it has the advantages of imparting no color to vulcanized rubber, and of giving a good plateau effect, good aging, and a low cost. Products containing such combinations of hexamethylenetetramine have been described in numerous articles and have appeared on the market, and it is needless to discuss them here.

Accelerators which have been extensively used with hexamethylenetetramine are thiocarbanilide, anhydroformaldehyde-*p*-toluidine, mercaptobenzothiazole and dibenzothiazole disulfide, among which mercaptobenzothiazole is known to form a combination of the ultra-accelerator class, with the merits of not too rapid vulcanization at the beginning and a good plateau effect. The present paper deals with many practical problems such as to what extent is the combination of hexamethylenetetramine and mercaptobenzothiazole superior, and what is the best ratio of these two to obtain the ideal results. An attempt is made to explain the reason why the combination of these two is so advantageous.

II. Experiment on the Combined Use

1. *Preparation of Samples.*—Hexamethylenetetramine was purified by the method of Akai and Kataoka (*J. Pharm. Soc. Japan*, **50**, 855 (1930)) from a commercial product; it was dissolved in absolute alcohol, the insoluble substance was filtered off, the crystals separated from the mother liquor on cooling were recrystallized from absolute alcohol, washed with ether once and dried *in vacuo* at 80° for 5 hours. The purity according to the method of Haze (*Pharm. Ztg.*, **52**, 851 (1907); *Deutsch-Am. Apotheker Ztg.*, **1907**, No. 7) was 99.96%.

Mercaptobenzothiazole was recrystallized twice from hot distilled water, and was then recrystallized once from benzene. The melting point of the product was 179–180.4° (by the capillary method).

2. *Vulcanization Experiments.*—The samples prepared in the preceding experiment were mixed in different proportions to test their accelerating effects.

Seven hundred grams of each mixture were milled on rolls at 60–65° C., and the accelerator, zinc oxide, and sulfur were added successively during 40 minutes, the mixtures were left at 8–15° C. for 24 hours, then vulcanized in steam at 20 lbs. (126°) and 40 lbs. (141°) per sq. in. The vulcanizates were left at room temperature (10–15°) for 48 hours, after which tensile strength, elongation, and modulus were determined on a Lewis-Schopper machine, using ring test-pieces. The results are given in Figs. 1 and 2.

3. *Scorching Experiment.*—Samples for scorching tests were compounded as in Table II. Mercaptobenzothiazole and hexamethylenetetramine were obtained from the sample prepared in Experiment 1.

Each sample was prepared by adding to 100 grams of rubber the accelerator, zinc oxide, and sulfur on a mill with the rolls at 55–60° C.

The milled samples were then pressed to 1 mm. thickness, left for 30 minutes at room temperature (10–15°), and tested for their scorching tendency. This test was

TABLE I

MIXINGS FOR VULCANIZATION TESTS

Sample No.	Pale Crepe	Zinc Oxide	Sulfur	Accelerator	Accelerator Ratio % Mercapto-benzothiazole	% Hexamethyl-enetetramine
1	100	5	3	1	100	0
2	100	5	3	1	90	10
3	100	5	3	1	80	20
4	100	5	3	1	70	30
5	100	5	3	1	60	40
6	100	5	3	1	50	50
7	100	5	3	1	40	60
8	100	5	3	1	30	70
9	100	5	3	1	20	80
10	100	5	3	1	10	90
11	100	5	3	1	0	100

made by heating flat circular pieces of 1.6-cm. diameter at 100° for a specified time leaving for 30 minutes, and shaking up and down in a test tube containing 50 cc. of gasoline, at the rate of 300 times per minute. The turbidity produced by zinc oxide in the gasoline was measured by estimating the reciprocal turbidity with a cuprous photo-electric cell at room temperature (10—15°). The distance between the source of light and the cuprous photo-electric cell was regulated so that the

TABLE II

COMPOUNDS FOR SCORCHING TEST

Sample No.	Pale Crepe	Zinc Oxide	Sulfur	Accelerator	Accelerator Ratio Mercapto.	Hexa.
1	100	100	3	1	100	0
2	100	100	3	1	90	10
3	100	100	3	1	80	20
4	100	100	3	1	70	30
5	100	100	3	1	60	40
6	100	100	3	1	50	50
7	100	100	3	1	40	60
8	100	100	3	1	30	70
9	100	100	3	1	20	80
10	100	100	3	1	0	100

deflection of the galvanometer remained at 28. The density of gasoline used for the test was 0.735–0.739 at 15°. The results are given in Fig. 3.

4. *Summary of the Experiments with Combined Accelerators.*—In Experiments Nos. 1, 2, and 3, the following facts were found:

(1) In vulcanization by steam at 40 lbs. per sq. in. (141°), the combined use of mercaptobenzothiazole and hexamethylenetetramine increased the tensile strength and accelerated vulcanization, compared with the single use of the accelerators, so that an optimum vulcanization was reached within 10 minutes in all cases.

(2) In vulcanization at 40 lbs. per sq. in. (141°), the modulus at 500 per cent elongation with mercaptobenzothiazole, either alone or in combination, was higher than with hexamethylenetetramine alone; and the moduli of mercaptobenzothiazole alone and in combination, were nearly identical.

(3) The percentage elongations of samples vulcanized at 40 lbs. steam per sq. in. were slightly lower with either hexamethylenetetramine or mercaptobenzothiazole alone, than with combinations of the accelerators; the values were in all cases not lower than 700 per cent.

(4) Since the tests after vulcanization at 40 lbs. per sq. in. did not show clearly which combination of accelerators was best, vulcanization at 20 lbs. steam (126°) per sq. in. was studied.

(5) Judged by the tensile strength curves of samples vulcanized at 20 lbs. steam

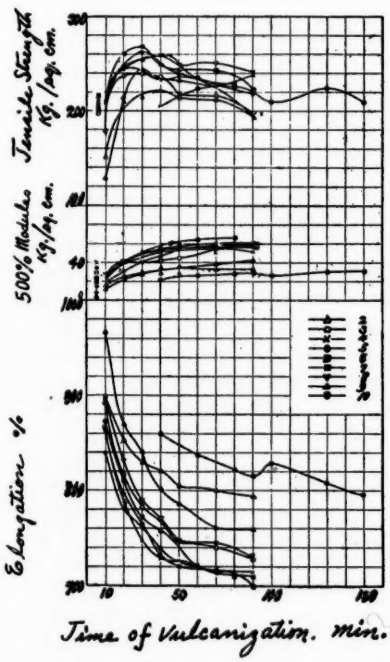


Figure 1. Vulcanization at 40 Lbs. per Sq. In.

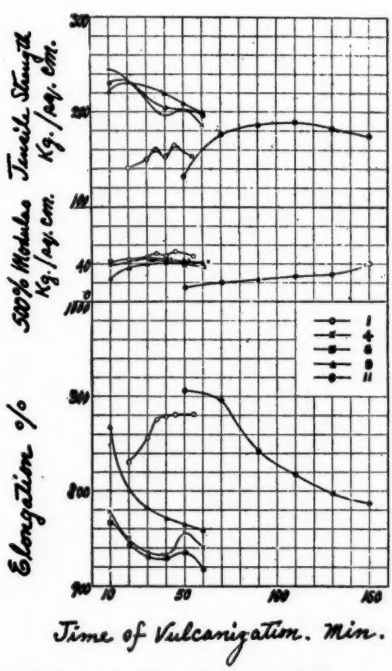


Figure 2. Vulcanization at 20 Lbs. per Sq. In.

per sq. in., the speed of vulcanization and tensile strength increased with increase in the hexamethylenetetramine/mercaptobenzothiazole ratio, to a maximum value with No. 6 which contained equal quantities. The tensile strength was lower in No. 7 (mercaptobenzothiazole 40, hexamethylenetetramine 60), the rate of vulcanization diminished and a pronounced plateau effect was obtained with No. 11 which contained hexamethylenetetramine only.

(6) The curves of the moduli at 500 per cent elongation after vulcanization by steam at 20 lbs. per sq. in. (126°) were nearly identical curves with the tensile strength curves. In general, No. 7 (mercapto. 40, hexa. 60), No. 6 (equal weights, and No. 8 (mercapto. 30, hexa. 70) gave the highest values.

(7) The elongation curves of samples vulcanized by steam at 20 lbs. per sq. in.

(126°) gave values similar to the tensile strengths. No. 4 (mercapto. 70, hexa. 30), No. 5 (mercapto. 60, hexa. 40), and No. 6 (equal amount of each) gave the lowest values, but even the lowest value was not below 700%.

(8) In the scorching test at 100°, hexamethylenetetramine alone was the slowest and mercaptobenzothiazole alone next; combinations of these showed a slight

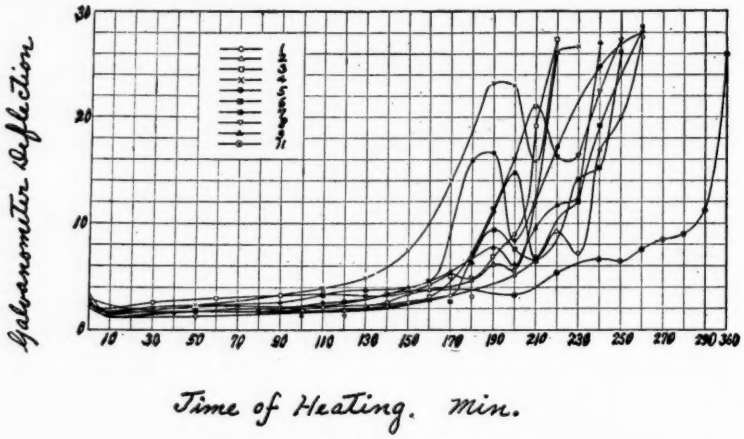


Figure 3. Scorching Test at 100°

tendency to scorch. The tendency to scorch was increased with an increase in the hexamethylenetetramine/mercaptobenzothiazole ratio. It was greatest with No. 4 (mercapto. 70, hexa. 30), and became slower with increase in the proportion of hexamethylenetetramine. In practice, however, there would be no danger of scorching, since No. 4 scorched in 120–130 minutes at 100°, but all other combinations scorched slowly after 170 minutes.

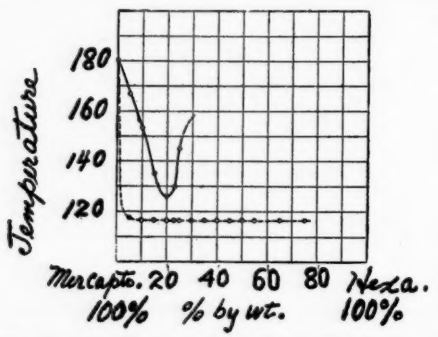


Figure 4. Melting and Softening Point Curves

(9) In summarizing, the combined use of hexamethylenetetramine and mercaptobenzothiazole did not impair the elongation, and increased the tensile modulus, and accelerated the vulcanization, with some plateau effect. In spite of these effects, the scorching tendency with the combined accelerators was low. The percentage elongations of samples with combined accelerators were not less than 700 per cent, the tensile strengths reached 270 kg. per sq. cm. and the optimum time of vulcanization was 10 minutes at 40 lbs. per sq. in. and 30 minutes at 20 lbs. per sq. in. With the proper selection of a ratio for these two accelerators, the scorching tendency can be so regulated that only mild scorching will take place around 170 minutes at 100°.

(10) Since they have such merits, combinations of these two accelerators have the highest practical value, especially when in a ratio of 1:1 as in No. 6, which gives an ideal acceleration, increases the tensile strength, and has a slow rate of scorching.

III. The Relation between the Melting Point of the Combined Accelerators and the Results Obtained with Them

1. *Formation of Melting Point Curve.*—Hexamethylenetetramine and mercaptobenzothiazole were purified as described in II—1. They were weighed in the ratios indicated in Table VI, ground together and the softening and melting points determined. The result is shown in Table III and Fig. 4.

TABLE III

SOFTENING AND MELTING POINTS

Ratio of Mixing		Softening Point,°	Melting Point,°
Mercaptobenzothiazole	Hexamethylenetetramine		
100	0	179.0	180.4
95	5	117.6	166.9
90	10	116.5	153.5
85	15	116.5	135.0
80	20	116.5	126.3
77	23	116.5	129.6
75	25	116.5	145.0

Mixtures containing over 25 per cent hexamethylenetetramine were dark colored and decomposed violently, so melting-point determinations were impossible; moreover hexamethylenetetramine sublimes slowly above 100°. However, the data obtained showed that the softening and melting points were closest with 80 per cent of mercaptobenzothiazole and 20 per cent of hexamethylenetetramine and that this mixture had the lowest melting point. The mixtures around this ratio showed no eutectic point. The data indicate that no molecular compound is formed; therefore there is no eutectic point.

2. *The Effect of Lowering of the Melting Point on Practical Problems.*—The effect of the lowered melting point was slight, but this was due to the change in their properties by the heating and not to the action of these mixtures as a binary system. The results show that there is some connection between the fact that there is the greatest tendency to scorch at above or below the ratio in sample No. 4 (mercapto. 70, hexa. 30) and the fact that the lowering of the melting point is most pronounced at around a ratio of mercaptobenzothiazole 80 and hexamethylenetetramine 20. It is surprising to find that the lowering of the melting point influences the scorching, yet has practically no influence on vulcanization. Since, however, the temperature of vulcanization is slightly higher than the temperature of scorching, the melting point curve of the binary system of the combined accelerators plays no part, since there is a change in composition at this temperature.

The binary system of these accelerators is thus very unstable, and decomposes on heating. Accordingly, only a part of the scorching test in II can be explained by the melting point curve, but all other results must have some other explanation. Moreover, even the melting point curve itself cannot depend completely on a change in composition or on sublimation by heating, though these changes become less as the proportion of mercaptobenzothiazole increases.

IV. Studies of the Decomposition Reaction and the Decomposition Products of the Accelerators during Vulcanization

1. *Studies of the Decomposition Reaction of the Accelerators by Means of the Heating Curve.*—As has been stated, the mechanism of acceleration by the combined accelerators cannot be explained by their melting point curve, or by the fact that the combined accelerators cause considerable decomposition during vulcanization. In

an attempt to discover a general tendency in the decomposition reaction of the accelerators, heating curves were made in the following way:

A sample composed of 6 grams of mixed accelerators was placed in a glass tube 1.6 cm. in diameter and 20 cm. long, and a thermometer was inserted in the center of sample. The system was then placed in an oil bath at 150° C. and readings were made every 15 seconds.

The reactions between these accelerators alone as well as with the addition of sulfur were studied. Sample No. 1 contained 50 per cent mercaptobenzothiazole and 50 per cent hexamethylenetetramine; No. 2, 50 per cent mercaptobenzothiazole and 50 per cent sulfur; No. 3, 50 per cent hexamethylenetetramine and 50 per cent sulfur. The accelerators were purified as before.

The results are shown in Fig. 5.

The deviations of temperature in No. 1 and No. 2 from the temperature of the bath were only slight, if even existent, but with No. 3 there was around 150° for the first 20 minutes a sudden rise in temperature, which reached a maximum of 170.5° in 23 minutes, after which it gradually dropped to the temperature of the bath in 27 minutes, indicating that there was an exothermic reaction during this time. The odor of gases evolved was noticeable after 10 minutes' heating, and the evolution increased after 20 minutes and became disagreeable. Following this the evolution of gases and the odor became less after 24 minutes.

It seems that there is a reaction, and that a part of the decomposition product is gas. To confirm if such a reaction takes place when the ratio of hexamethylenetetramine and sulfur is changed, the following samples were tested: No. 4 (1:3), No. 5 (2:1).

Figure 6 indicates that both gave nearly the same result as in the case of No. 3; there was practically no difference in the heating curves when the ratio of hexamethylenetetramine and sulfur was changed.

With practical vulcanization in mind, the heating curve of the ternary system of M, H, and S was studied. Since the preceding experiment showed that the propor-

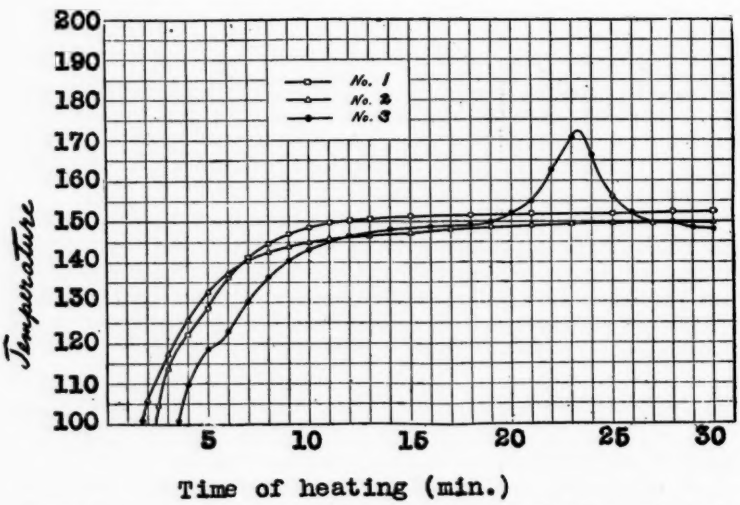


Figure 5. Temperature Curves of Mercaptobenzothiazole + Hexamethylenetetramine, Mercaptobenzothiazole + Sulfur and Hexamethylenetetramine + Sulfur by Heating at 150°

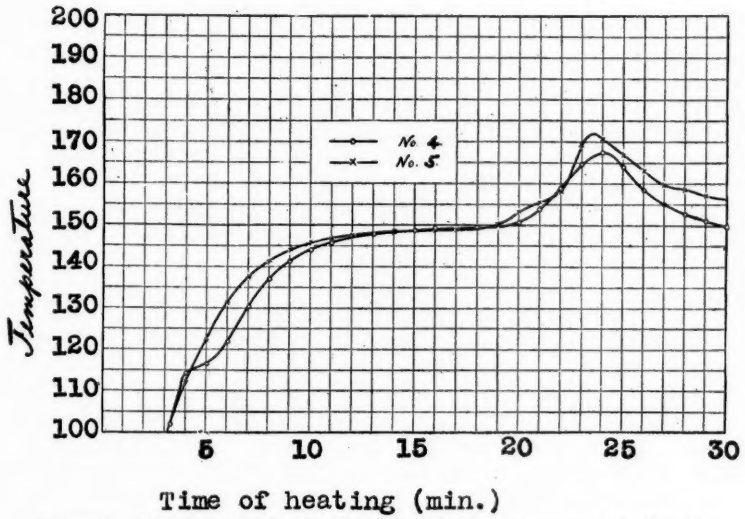


Figure 6. Temperature Curves of Hexamethylenetetramine + Sulfur by Heating at 150°

tion of S had no effect on the heating curve, the ratios of mercaptobenzothiazole and hexamethylenetetramine were changed, keeping a constant proportion of S, thus:

Sample No.	Pure Mercaptobenzothiazole %	Pure Hexamethylenetetramine %	Sulfur %
6	40	10	50
7	30	20	50
8	20	30	50
9	10	40	50

The heating curves of samples are given in Table IX and Fig. 7.

As all samples contained hexamethylenetetramine, mercaptobenzothiazole, and sulfur, each curve had one exothermic point, as in samples No. 4 and No. 5, but it is interesting to note that an exothermic reaction appeared in a shorter time with more mercaptobenzothiazole. This may, as will be described later, be due to an absorption of ammonia gas evolved from the decomposition of hexamethylenetetramine and sulfur by the mercaptobenzothiazole, which acts as a catalyst of the reaction between hexamethylenetetramine and sulfur. Accordingly, it is important not to overlook the catalytic action of mercaptobenzothiazole when the exothermic reaction of hexamethylenetetramine and sulfur is considered of advantage.

2. *Analysis of the Reaction Products from Hexamethylenetetramine and Sulfur.*— It is thus proved by the evolution of heat that hexamethylenetetramine and sulfur react during vulcanization and that the reaction is accelerated by the presence of mercaptobenzothiazole. It is known, as indicated in the references in IV, that the reaction products from hexamethylenetetramine and sulfur are NH_3, H_2S, CS_2, HCNS, etc. The authors not only confirmed qualitatively the presence of these products, but also attempted quantitative analyses, with the idea that analysis of large numbers of samples even in a rough way might give more imformation on the reaction than would an accurate analysis of a few samples.

The test tube containing the sample was connected to a Liebig condenser (in horizontal position) and to a series of Peligot-Robertson U tubes containing 1*N*

H_2SO_4, 10% aqueous NaOH, concentrated H_2SO_4, and 2*N* alcoholic KOH in the order named. A six-gram sample was placed in a glass tube and heated at 150° in an oil bath for 0.5, 1, 2, and 4 hours, respectively. Gases such as NH_3, H_2S, and CS_2 were estimated, and the volumes of gas evolved and the loss on heating were estimated from the loss in weight and the thiocyanate value of the residue as NH_4-CNS. The change in weight and the gaseous products formed in relation to the time of heating are shown in the graph.

The methods of analysis of these reaction products were as follows. *Ammonia.*—The NH_3 evolved was passed through 1*N* H_2SO_4 and this was titrated back with 1*N* KOH. *Hydrogen Sulfide.*—After removal of ammonia, the gas was passed through 10% KOH, to this sufficient standard iodine and dilute hydrochloric acid were added, the H_2S was decomposed to free S and HI by oxidation, and excess iodine was titrated back by standard sodium thiosulfate. *Carbon Disulfide.*—After absorption of H_2S, the gas was passed through 2*N* alcoholic KOH, caught as potassium xanthate, neutralized with dilute acetic acid and titrated by oxidation with standard iodine after addition of sodium bicarbonate (cf. Rodcliffe, *J. Soc. Chem. Ind.*, **28,** 229 (1909)). *Ammonium Thiocyanate.*—After heating the original sample, the residue was dissolved in aqueous KOH and 0.5*N* $Pb(NO_3)_2$ added to precipitate the remaining H_2S and mercaptobenzothiazole as lead salts, which were filtered. The residue was washed with dilute HNO_3 to dissolve $Pb(CNS)_2$, and the filtrate was titrated with 0.1*N* $AgNO_3$, with ferric nitrate as indicator (Minatoya, Nagai, and Aoe, *J. Soc. Rubber Ind. Japan*, **7,** 123 (1934)).

The first sample was a mixture of 0.5 gram hexamethylenetetramine and 1 gram of sulfur. The results are given in Fig. 8.

A ternary system consisting of 0.25 gram of pure hexamethylenetetramine, 0.25 gram of pure mercaptobenzothiazole, and 0.5 gram of sulfur was then tested, with the results indicated in Fig. 9.

Figures 8 and 9 indicate that the weights of the reaction products from hexamethylenetetramine and sulfur decreased in the order: CS_2, NH_4CNS, H_2S, and NH_3. The formation of CS_2 and H_2S increased for 4 hours with increase in the time of heating; the formation of NH_3 is very slight.

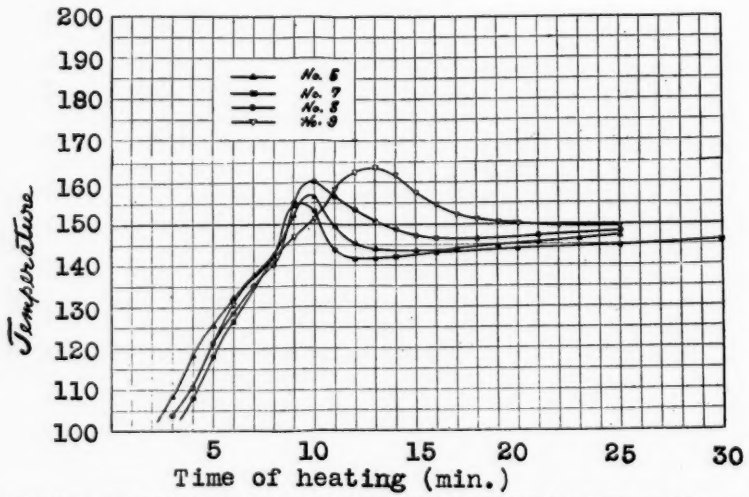


Figure 7. Temperature Curves of Mercaptobenzothiazole + Hexamethylenetetramine + Sulfur by Heating at 150°

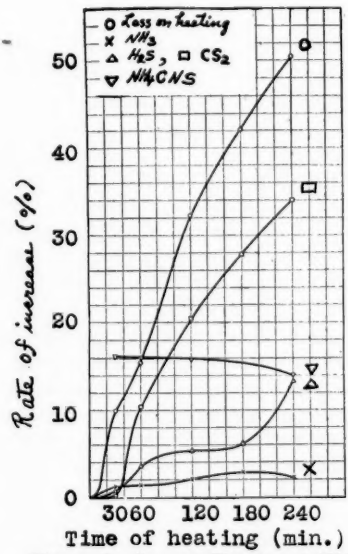


Figure 8. Loss on Heating at 150° of the System Hexamethylenetetramine Sulfur and the Rate of Increase of the Products of Reaction

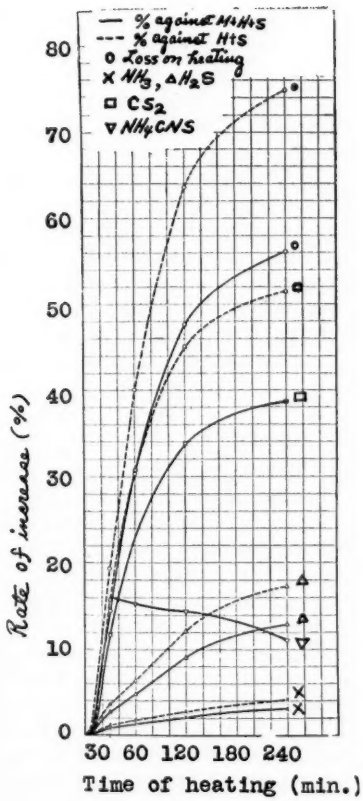


Figure 9. Loss on Heating of the System, Mercaptobenzothiazole-Hexamethylenetetramine-Sulfur, and the Rate of the Reaction Products during the Heating

NH_4CNS showed a rapid increase, then gradually decreased, probably because of decomposition by heating. The loss of weight by heating was very rapid, and it increased linearly with increase in time, reaching around 50 to 60%. With mercaptobenzothiazole in addition to hexamethylenetetramine and sulfur, the formation of CS_2 and of H_2S is greater at the beginning of heating than in a system containing no mercaptobenzothiazole. By increasing the proportion of sulfur, practically the same result was obtained as that by increasing the time of heating, though the data of these experiments are not given in the table.

The time required for a rapid evolution of CS_2 and H_2S for the sample containing mercaptobenzothiazole was one-half that of the sample without mercaptobenzothiazole. It is interesting to note these facts and the preceding experiment, in which the time required to show the first exothermic reaction for the sample with mercaptobenzothiazole was one-half that of the sample without it. These facts prove that mercaptobenzothiazole acts as a catalyst in the reaction of hexamethylenetetramine and sulfur.

The formation of NH_3 was very slight; and it may probably be due to the formation of NH_4CNS which is left in the residue.

These analytical data, however, are made from rough estimations, and therefore the data cannot be expressed in chemical equations.

V. The Mechanism of the Reaction of Accelerators during the Vulcanization Process and an Explanation of the Effect of Using Combined Accelerators

Since the preceding experiment indicated that the efficiency of the combined accelerators might have been due principally to the reaction products from hexamethylenetetramine and sulfur, it is necessary to review briefly the literature concerning the products of reaction between hexamethylenetetramine and sulfur, and the mechanism of acceleration by these products.

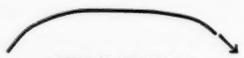
Dubosc (*India Rubber World*, **59**, 248 (1919)) stated that the efficiency of hexamethylenetetramine in vulcanization is due to the formation of H_2S and HNCS from the reaction between hexamethylenetetramine and sulfur thus:

$$(CH_2)_6N + 9S \longrightarrow 4(CNHS) + 3H_2S + C_2H_2$$

A subsequent experiment by Dubosc (*India Rubber World*, **63**, 174 (1920)) proved that heating of hexamethylenetetramine and sulfur in a sealed tube at 135–145° forms HNCS as well as CS_2 and H_2S, and bivalent S in HNCS forms hexavalent free sulfur during vulcanization thus: $HCNS \rightleftarrows HCN + S$; the hexavalent sulfur thus liberated takes part in the vulcanization process.

Scott and Bedford (*Ind. Eng. Chem.*, **13**, 125 (1921)) explained that CS_2 and NH_3 are produced during vulcanization by hexamethylenetetramine, and either CS_2 or both may react with the amines in the raw rubber to form a salt of dithiocarbamic acid, and this product acts as a vulcanization accelerator. Another explanation is that H_2S formed in the heating of hexamethylenetetramine and sulfur may react with ammonia to form ammonium polysulfide, which may be an accelerator. Thus Scott and Bedford concluded that acceleration with hexamethylenetetramine may be explained by the presence of 2 groups, RS_x and $\equiv CSH$.

2. *Mechanism of Vulcanization Acceleration by the Products of the Reaction between Hexamethylenetetramine and Sulfur and Its Efficiency with Mercaptobenzothiazole.*—The authors obtained CS_2, H_2S, NH_3, and NH_4CNS as products of the reaction between hexamethylenetetramine and sulfur in the preceding experiment, and found that these products are related to acceleration as reported in the literature. The possible chemical reactions and the products of the reaction between hexamethylenetetramine and sulfur are:



(1) $S + C_6H_{12}N_4 \longrightarrow NH_2C(S)SNH_4 \longrightarrow S, NH_3, H_2S, CS_2, NH_4CNS$
(2) $CS_2 + 2NH_3 = NH_2C(S)SNH_4$
(3) $NH_2C(S)SNH_4 + 2NH_3 = NH_4CNS + (NH_4)_2S$
(4) $2NH_3 + H_2S = (NH_4)_2S$
(5) $NH_4CNS \rightleftarrows H_2NCSNH_2$

Among these reaction products, CS_2 or H_2S itself probably has no marked influence on the efficiency of mercaptobenzothiazole. Since the accelerating efficiency of NH_4CNS is not clear, vulcanization tests of mixtures containing: rubber 100, zinc oxide 5, and sulfur 3, and NH_4CNS 1–2, were vulcanized by steam at 40 lbs. per sq. in. for various times. All of the products were incompletely vulcanized, indicating that NH_4CNS is a poor accelerator. NH_4CNS changes to $SC(NH_2)_2$ at a high temperature. Bedford and Scott (*Ind. Eng. Chem.*, **12**, 31 (1920)) believed that the mechanism of acceleration of hexamethylenetetramine is due to the forma-

tion of thiourea, thus: $NH_3 + CS_2 \longrightarrow SC(NH_2)_2$. This is probably based on the equilibrium: $NH_4CNS \rightleftharpoons SC(NH_2)_2$, but this equilibrium predominates above 170° and is not possible at the low temperature of the experiment above. Moreover, the formation of thiourea in this way has not been experimentally proved.

The theory of Bedford and Scott of dithiocarbamate formation from CS_2 and NH_3 is proved by the authors' synthesis from CS_2 and NH_3; *e. g.*, treatment of alcoholic CS_2 with excess 2*N* alcoholic NH_3, letting stand overnight, filtering the precipitate and drying at room temperature, gives light yellow crystals. The crystals melted at 102–105.8° (at 105.8° they decomposed with foaming), and contained 60.07 per cent sulfur. Since the sulfur content of $SC(NH_2)_2$ is 60.38 per cent, they must have been ammonium thiocarbamate. Addition of 1 part of this product to 100 parts of raw rubber, 5 parts of zinc oxide, and 3 parts of sulfur, and vulcanization by steam at 30 lbs. per sq. in. (134.5°) for 70 minutes, showed however no indication of vulcanization, accordingly, this substance must be of an extremely poor accelerator. Therefore, this result did not agree with the theory of Scott and Bedford.

When aqueous ammonium thiocarbamate was made slightly acid by hydrochloric acid and was oxidized by ferric chloride, it gave a white crystalline precipitate, which, filtered and dried *in vacuo*, gave a light yellow crystalline substance which was extremely unstable and could not be purified. It was probably the thiuram disulfide, $NH_2C(:S)SSC(:S)NH_2$. Addition of one part of this product to 100 parts of raw rubber, 5 parts of zinc oxide and 3 parts of sulfur, and vulcanization by steam at 30 lbs. (134.5°) per sq. in. for 50 min. showed no evidence of vulcanization. Therefore, this product also has no accelerating activity.

In summarizing the above experiments, CS_2, H_2S, NH_4CNS, etc., or their newly formed derivatives formed in the reaction of hexamethylenetetramine and sulfur had no accelerating power, and it is difficult to explain the mechanism of acceleration by mercaptobenzothiazole with the aid of these products.

In the reaction products of hexamethylenetetramine and sulfur, ammonia and ammonium polysulfide have not been discussed. The vulcanization efficiency of ammonia has been known for a long time, and there are many patents. Ammonia alone is a poor accelerator. Ammonium polysulfide as an accelerator has also been described numerous times, and it is reported to be a poor accelerator (Kratz, Flower, and Shapiro (*Ind. Eng. Chem.*, **13**, 67 (1921)). Studies were first made of these reaction products, after which the effect of addition of mercaptobenzothiazole will be studied.

A mixture of raw rubber 100, zinc oxide 5, and sulfur 3, was pressed to 3 mm. thickness, and was immersed in concentrated aqueous ammonia and in ammonium polysulfide for 2–3 hours. It was then removed and vulcanized in steam at 30 lbs. per sq. in. for 1 hour. There was no evidence even of under-vulcanization.

In the next experiment, a similar mixture containing also 0.5 part of mercaptobenzothiazole was treated in the same way and vulcanized for 5 min. In this case vulcanization took place, showing that ammonia and ammonium polysulfide from the reaction between hexamethylenetetramine and sulfur are very effective with mercaptobenzothiazole. A preliminary test of vulcanization with NH_4CNS and $NH_4SC(:S)NH_2$ with mercaptobenzothiazole showed that there was no such marked vulcanization efficiency.

3. *Increase in the Vulcanization Efficiency of Mercaptobenzothiazole by Ammonia.*—In the preceding report, Minatoya, Kojima, and Nagai (*J. Soc. Rubber Ind. Japan*, **3**, 71 (1931)) showed that the accelerating power of combinations of acidic substances, such as mercaptobenzothiazole, and a basic substance, such as diphenylguanidine, depends on the formation of a molecular compound which has far greater accelerating activity than its components. The formation of a molecular compound

from ammonia and mercaptobenzothiazole is also possible. U. S. Patent No. 1,613,574 (1927) of Bedford claims that treatment of raw rubber, sulfur, zinc salt of mercaptobenzothiazole and zinc oxide mixtures with gaseous ammonia gives an ultra-acceleration effect, whereas without the ammonia gas the accelerating power is slight. In view of these facts, the authors made the following experiment. The zinc salt of mercaptobenzothiazole in the above patent was replaced by mercaptobenzothiazole and zinc oxide. A mixture of crepe 100, zinc oxide 5, sulfur 3, and pure mercaptobenzothiazole 1, was pressed to 6–7 mm. thickness and placed on a

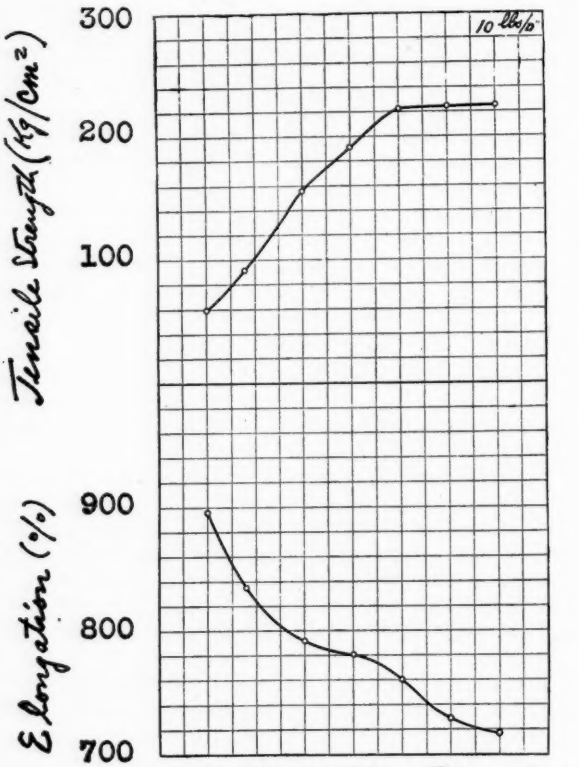


Figure 10. Vulcanization Test on Sample Containing Mercaptobenzothiazole with Ammonia Gas

wire gauze. It was then placed in a tin box containing 100-cc. concentrated ammonia and covered so that there could be free contact with ammonia gas on both sides. It was left thus for 70 hours. The sample thus treated was vulcanized by steam at 10 lbs. per sq. in. (115°) for various times up to 40 minutes. The tensile strengths and percentage elongations determined as described in II, 2, are given in Fig. 10.

The tensile strength of the sample vulcanized at 10 lbs. per sq. in for 25 minutes was more than 200 kg. per sq. cm. and the acceleration was far greater than with

mercaptobenzothiazole alone, in fact the activity was of the ultra-accelerator class, and this activity was entirely brought about by the treatment with ammonia. It is difficult to isolate the ammonium salt of mercaptobenzothiazole in the laboratory, but it is likely that mercaptobenzothiazole forms a molecular compound with ammonia as in the case of mercaptobenzothiazole and diphenylguanidine, and this molecular compound increases the accelerating power.

Let the above theory be applied to the combined use of hexamethylenetetramine and mercaptobenzothiazole. Ammonia is evolved from the reaction of hexamethylenetetramine and sulfur, and ammonia further reacts with mercaptobenzothiazole to form a molecular compound. The fact that ammonia is not evolved at low temperatures and there is no tendency of the mixtures to scorch agrees with the experimental data. The preceding experiment shows that the combined use of ammonia or ammonium polysulfide with mercaptobenzothiazole is effective. The following equilibria exist in the systems of the reaction of NH_3, H_2S, and sulfur.

$$NH_3 + H_2S \rightleftharpoons NH_4HS$$
$$NH_4HS + NH_3 \rightleftharpoons (NH_4)_2S$$
$$(NH_4)_2S + xS \rightleftharpoons (NH_4)_2S_{(x+1)}$$

There is an equilibrium in each system, and the ammonium polysulfide thus formed may be decomposed by H_2S, NH_3, or sulfur. In other words, the activity of mercaptobenzothiazole with ammonium polysulfide is attributed to mercaptobenzothiazole and ammonia. The preceding vulcanization experiments on the combination of accelerators explain well this activity.

VI. Conclusions

In the combined use of hexamethylenetetramine and mercaptobenzothiazole, a mixture of equal parts by weight gave the minimum tendency to scorch, gave the highest acceleration, did not give a low elongation, gave the maximum tensile strength, and gave a high plateau effect.

This activity is explained by the formation of a molecular compound from mercaptobenzothiazole and ammonia, the latter of which is formed from the reaction between hexamethylenetetramine and sulfur. Ammonia in this case is not generated from the beginning of the vulcanization process, but is evolved with an increase in the temperature. This type of vulcanization accelerator is already in the market, *e. g.*, Z-88 (Rubber Service Laboratories Company) is a fused mass of mercaptobenzothiazole and hexamethylenetetramine. Numerous commercial accelerators are an improvement of this combination (cf. Fabriziev and Schabanova: *Rev. gen. caout.*, **10,** June, 1933). It is also of interest to mention U. S. Patent No. 1,613,574 (1927) of Bedford, which involves treating a mixture of rubber, mercaptobenzothiazole, zinc oxide and sulfur with ammonia gas. Vulcanization can then be made in a short time, the quality is good, and there is no danger of scorching. Replacement of mercaptobenzothiazole by dibenzothiazole disulfide, tetraalkylthiuram disulfide or zinc tetraalkyldithiocarbamate, as stated in its specification, gives still less danger of scorching and increase in accelerating power.

This method, however, cannot be applied to the vulcanization of a thick sheet, since the penetration of ammonia is difficult, but it is particularly suitable for the continuous vulcanization of a thin sheet.

VII. Summary

1. Equal weights of a mixture of hexamethylenetetramine and mercaptobenzothiazole give the optimum accelerating activity and minimized scorching.

2. Scorching tests indicate that there should be no danger of scorching in practice; a comparison of the scorching tendencies of various proportions showed that a ratio of mercaptobenzothiazole 70 and hexamethylenetetramine 30 gives noticeable scorching.

3. The melting point curves, indicate some relation between the above proportion and the scorching phenomenon.

4. The heating curves of two sets of mixtures containing hexamethylenetetramine and sulfur, and hexamethylenetetramine, mercaptobenzothiazole and sulfur, respectively, in an oil bath at 150°, indicate that hexamethylenetetramine and sulfur react exothermically and that this reaction is accelerated by the presence of mercaptobenzothiazole.

5. The products of the reaction between hexamethylenetetramine and sulfur are carbon disulfide, ammonium thiocyanate, hydrogen sulfide, and ammonia.

6. The products of the reaction of two sets of samples heated in an oil bath at 150°, as indicated in 4, were determined quantitatively, and it was found that there was an increase of these products with an increase of time; which was also indicated by the loss of weight during the heating.

7. All of these reaction products had low accelerating power. Thiuram disulfide and ammonium thiocarbamate derived from carbon disulfide and ammonia and ammonium polysulfide derived from hydrogen sulfide, ammonium, and sulfur were tested, since they might have been formed during vulcanization, but they were found to be poor accelerators.

8. A preliminary test of combinations of mercaptobenzothiazole with ammonia, ammonium polysulfide, ammonium thiocyanate, and ammonium dithiocarbamate indicated that ammonia and ammonium polysulfide have some accelerating power, whereas all others are ineffective.

9. The combined use of ammonia and mercaptobenzothiazole forms a molecular compound which is effective as an accelerator, and this is true in an analogous way of the combined use of hexamethylenetetramine and mercaptobenzothiazole.

10. In order to prove experimentally the above theory, an attempt was made to treat a mixture of rubber, mercaptobenzothiazole, zinc oxide and sulfur with ammonia until the latter penetrated throughly the sample, after which the latter was vulcanized. Such treatment gives far better acceleration than does mercaptobenzothiazole without treatment with ammonia.

11. The accelerating power of ammonium polysulfide and mercaptobenzothiazole is attributed to the formation of ammonia from ammonium polysulfide and the reaction of ammonia and mercaptobenzothiazole.

The present work has been published with the permission of W. Ogawa, chief of the Fifth Department. The authors wish to thank S. Minatoya for his kind advice during the course of this investigation.

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Studies on the Acetone Extraction of Raw Rubber

V. The Influence of Heating at 100° C. and Storage of the Acetone Extract on the Saponification Value

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The influence of heating the acetone extract at 100° C. and of storage on its saponification value was studied.

(*A*) The relation between the time of heating the acetone extract at 100° C. and the saponification value.

The acetone extract was obtained as previously described. In view of the results obtained in the previous work, drying was carried out for as short a time as possible, usually for 3 minutes. After the flasks were cooled and weighed, they were heated in a steam bath for 0, 15, 30, and 60 minutes, respectively, and the saponification values were determined.

(*a*) Acetone extract from 8 hours' continuous extraction.

Table I

Sample (5 sheets) 8.1283 grams

Acetone extract (g.) A_0	0.0564	0.0522	0.0572	0.0508
Acetone extract (%)	3.47	3.21	3.51	3.13
Time of heating (min.)	0	15	30	60
Acetone extract after heating (g.) A_T	0.0564	0.0576	0.0576	0.0576
Acetone extract after heating (%)	3.47	3.54	3.54	3.54
0.1 *N* HCl (cc.)	1.3	1.35	1.4	1.35
Saponification value (A)	129.0	144.8	137.1	148.8
Saponification value (AT)	129.0	131.3	136.1	131.2
A_T/A_0 (%)	100.0	110.2	100.8	113.2
Saponification value (R)	4.48	4.65	4.82	4.65

In the above table the saponification value relative to the acetone extract after heating is expressed as saponification value (AT).

(*b*) Acetone extract from 16 hours' continuous extraction.

Table II

Sample (5 sheets) 7.5955 grams

Acetone extract (g.) A_0	0.0482	0.0452	0.0499	0.0454
Acetone extract (%)	3.17	2.98	3.29	3.00
Time of heating (min.)	0	15	30	60
Acetone extract after heating (g.) A_T	0.0482	0.0494	0.0468	0.0482
Acetone extract after heating (%)	3.17	3.26	3.08	3.15
0.1 *N* HCl (cc.)	1.5	1.5	1.5	1.5
Saponification value (A)	174.3	185.9	168.6	185.0
Saponification value (AT)	174.3	170.0	179.5	174.5
A_T/A_0 (%)	100.0	109.2	93.7	106.2
Saponification value (R)	5.54	5.54	5.54	5.54

(*c*) Acetone extract from 24 hours' continuous extraction.

TABLE III

Sample (5 sheets) 9.8924 grams

Acetone extract (g.) A_0	0.0710	0.0731	0.0720	0.0662
Acetone extract (%)	3.59	3.70	3.64	3.35
Time of heating (min.)	0	15	30	60
Acetone extract after heating (g.) A_T	0.0710	0.0746	0.0710	0.0668
Acetone extract after heating (%)	3.59	3.73	3.60	3.38
0.1 *N* HCl (cc.)	1.75	1.7	1.7	1.65
Saponification value (A)	138.0	130.2	132.2	139.6
Saponification value (AT)	138.0	127.7	133.7	138.3
A_T/A_0 (%)	100.0	102.1	98.9	101.0
Saponification value (R)	4.96	4.82	4.82	4.68

(*B*) The relation between the time of storage of the acetone extract and the saponification value.

(*a*) Storage of the acetone extract in a desiccator.

Acetone extract from pale crepe (8 hours' continuous extraction) was put in a $CaCl_2$-filled desiccator. The saponification value was determined after storing for 1, 2, and 3 days (not in a dark room).

TABLE IV

Sample (5 sheets) 8.4540 grams

Acetone extract (g.) A_0	0.0603	0.0602	0.0590	0.0640
Acetone extract (%)	3.57	3.67	3.49	3.79
Days extract stored	0	1	3	5
Acetone extract after storing (g.) A_T	0.0603	0.0594	0.0630	0.0590
Acetone extract after storing (%)	3.57	3.52	3.73	3.49
0.1 *N* HCl (cc.)	1.4	1.5	1.45	1.5
Saponification value (A)	130.0	135.5	137.6	131.2
Saponification value (AT)	130.0	141.5	128.9	142.4
A_T/A_0 (%)	100.0	95.8	106.9	92.1
Saponification value (R)	4.64	4.97	4.80	4.97

(*b*) The relation between storage of an acetone solution of the acetone extract and the saponification value.

Acetone extract from 8 hours' continuous extraction was used. Four stoppered flasks, each containing 50 cc. of an acetone solution of acetone extract, were stored in darkness at room temperature. After the required time the flasks were taken out, the acetone was evaporated, and the flasks were dried and weighed, after which the saponification value was determined.

TABLE V

Sample (5 sheets) 8.5528 grams

Acetone extract (g.) A_0	0.0604	.....	.....	.....
Acetone extract (%)	3.53	.....	.....	.....
Days extract stored	0	1	3	5
Acetone extract after storing (g.) A_T	0.0604	0.0599	0.0650	0.0650
Acetone extract after storing (%)	3.53	3.51	3.80	3.80
0.1 *N* HCl (cc.)	1.55	1.65	1.45	1.5
Saponification value (A)	143.7	153.0	134.5	139.2
Saponification value (AT)	143.7	154.3	124.9	129.1
A_T/A_0 (%)	100.0	99.2	107.8	107.8
Saponification value (R)	5.08	5.41	4.75	4.92

Summary of Results

(1) When the acetone extract was heated at 100° C., the saponification value (AT) first diminished and then increased.

(2) When the acetone extract was stored, the saponification value (AT) first increased and then diminished and returned to the original value.

(3) The determination of the saponification value was carried out as follows: The sample was extracted for the required time, the acetone was evaporated off as rapidly as possible and the flask was dried in a steam bath for as short a time as possible. The drying time must not be over 15 minutes, and usually 5 minutes is sufficient. The dried flask was cooled and weighed, after which 20 cc. of 0.2 *N* alcoholic KOH was added and the flask heated on a water bath for 60 minutes. The excess alkali was titrated with 0.1 *N* HCl solution, using phenolphthalein as indicator.

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Self-Vulcanizing Cements

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By self-vulcanizing cements is to be understood cements, films of which at regular room temperature assume within a period of one or two days a vulcanized state.

As implied by this definition, self-vulcanizing cements must be based on exceedingly active accelerators. The ultra-accelerators regularly used, such as thiuram disulfides, "Zimate," and so forth, are not suitable for the purpose. We tested them in our preliminary work, and have proved their inadequacy in this respect. Nevertheless the industry used, under the name of self-vulcanizing cements, cements based on these accelerators.

In self-vulcanizing cements accelerators with the lowest critical temperature must be used. Of those available, we chose Vulkacit P, Pipsol X, and zinc butylxanthate, and have established their critical temperature of vulcanization, with the following results:

Critical temperature for tetramethylthiuram disulfide	110° C.
Critical temperature for Vulkacit P	60° C.
Critical temperature for Pipsol X (American)	60° C.
Critical temperature for zinc butylxanthate	59° C.

On the basis of the above results, we chose zinc butylxanthate.

For an activator we used *p*-toluidine,* the critical temperature of the accelerator being lowered from 50° C. to 40° C. by the *p*-toluidine.

It was with this combination of zinc butylxanthate and *p*-toluidine that we carried out our next work on the following lines:

1. Development of a cement formula.
2. Testing the cement of the chosen formula under laboratory conditions by cementing leather specimens or canvas with rubber, and separating same after curing them in different conditions.
3. Study of gelling in the process of storing cements.

PART I

DEVELOPMENT OF CEMENT FORMULA BASED ON ZINC BUTYLXANTHATE AND *p*-TOLUIDINE

1. *Methods of Work.*—Preliminary tests of various samples of cement by separating cemented standard samples of leather and rubber showed that even when average values were obtained for a large number of tests this method is not sufficiently sensitive to reflect all possible variations in those properties of cement which depend upon changes in formula. For this reason we conducted this part of our work by a method which ensured considerably greater accuracy and speed, namely, testing the cements as films. The technic was as follows.

A certain quantity of rubber was plasticized on a laboratory mill for five minutes, then zinc oxide and sulfur were introduced. The stock from the mill was left for

* American Patent No. 1,440,962; 1923, January 2.

a day, after which an 8 per cent cement was made with benzene distilling within the range of 80° to 120° C.

Zinc butylxanthate in the form of a paste was then added by preliminarily mixing with a small amount of cement. *p*-Toluidine, which dissolves readily in benzene, was added directly to the cement. After the addition of the accelerator, the cement was left to settle for 12–18 hours, after which films were made from it.

The films were produced by dipping glass cylindrical formers of 2.5 to 3 cm. diameter in the cement four times. After each dipping the films were dried in the air at room temperature for 30–45 minutes, the surplus cement flowing down freely from the vertically suspended former. Films of a thickness varying from 0.18 to 0.20 mm. were thus obtained.

Forms with films were left in the air at 20° C. for one day, after which they were cured in distilled water at 80° C. for different periods of time. Vulcanized films were taken off the form, and cut into rings 8 mm. wide by means of punches. After a careful measurement of their thickness the rings were tested on a Schopper dynamometer, their tensile strength and elongation at break being ascertained.

2. *Investigation of the Activating Influence of Zinc Oxide, Stearic Acid, and Zinc Stearate on Zinc Butylxanthate.*—The following formulas of compounds were tested for the purpose of investigating the activating influence of zinc oxide, stearic acid, and zinc stearate:

	1	2	3	4	5	6	7
Smoked sheets	100	100	100	100	100	100	100
Sulfur	2	2	2	2	2	2	2
p-Toluidine	1	1	1	1	1	1	1
Zinc butylxanthate	1	1	1	1	1	1	1
Zinc oxide	0.5	2	3	4	5	3	
Stearic acid						1	
Zinc stearate							4

The mechanical tests of vulcanized films of the above-mentioned formulas are summarized in Table I.

TABLE I

Curing Time in Min.	Test	No. of Formula 1	2	3	4	5	6	7
30	Z	60	178	175	132	82	27	10
	L	830	916	910	890	910	850	550
	F	498	1629	1591	1171	746	229	55
40	Z	72	181	184	138	97	30	12
	L	834	900	930	895	898	820	650
	F	600	1627	1711	1206	871	246	78
50	Z	84	187	192	142	111	40	18
	L	871	972	930	872	890	790	700
	F	731	1629	1781	1237	989	315	126

Here, as in all the work, the following symbols are used:

Z = tensile strength in kg. per sq. cm.
L = elongation at break (in percentage)
F = tensile product (Z × L).

Table I shows that zinc oxide had a strong activating effect upon the vulcanization of films, the best mechanical properties being found in films having 3 per cent of zinc oxide.

Zinc stearate had no activating properties in relation to the butylxanthate.

Stearic acid diminished the strength of the film; *e. g.*, the tensile strength of formula No. 3, vulcanized for 50 minutes, was reduced by the introduction of 1 per cent of stearic acid from 192 to 40 kg. per sq. cm. (compare formulas 3 and 7).

3. *Study of Different Proportions of Sulfur.*—The compounds of the following formulas were tested for the purpose of discovering what effect sulfur has upon the rate of vulcanization of films:

	8	9	10	11	11a
Smoked sheet	100	100	100	100	100
Sulfur	2	3	2	3	4
Zinc oxide	3	3	3	3	3
Zinc butylxanthate	3	3	3	3	3
p-Toluidine	1	1	1.5	1.5	1.5

Table II summarizes the mechanical tests of vulcanized films of the above-mentioned formulas.

TABLE II

Duration of Cure in Min.	Test	No. of Formula 8	9	10	11	11a
20	Z					225
	L					856
	F					1920
30	Z				219	238
	L				813	802
	F				1780	1910
40	Z				243	230
	L				790	820
	F				1920	1885
50	Z		252		253	230
	L		847		865	828
	F		2130		2190	1905
60	Z	198	231	219	256	215
	L	878	883	909	815	818
	F	1740	2040	1990	2090	1760
70	Z	216		215		
	L	940		918		
	F	2030		1975		
80	Z	215		226		
	L	927		908		
	F	2020		2050		

As may be seen from Table II, an increase in sulfur from 2 per cent to 3 per cent tends to decrease the period of vulcanization, and increases the mechanical strength. An increase of 4 per cent further accelerates vulcanization, and reduces the mechanical strength. This is the reason why 3 per cent sulfur was chosen in all the experiments.

4. *Study of Different Proportions of Zinc Butylxanthate.*—The following formulas were used to ascertain the most suitable proportion of zinc butylxanthate.

	12	13	14	15	16
Smoked sheet	100	100	100	100	100
Sulfur	3	3	3	3	3
Zinc Oxide	3	3	3	3	3
Zinc butylxanthate	1	2	3	4	5
p-Toluidine	1.5	1.5	1.5	1.5	1.5

The mechanical tests of vulcanized films are summarized in Table III.

TABLE III

Curing time in min.	Test	No. of Formula 12	13	14	15	16
20	Z				242	236
	L				783	784
	F				1895	1840
30	Z			219	259	243
	L			813	744	798
	F			1780	1930	1940
40	Z			243	268	236
	L			790	755	847
	F			1920	2025	2000
50	Z		252	253	279	227
	L		847	865	772	780
	F		2130	2190	2150	1700
60	Z	109	231	256	277	
	L	926	883	815	778	
	F	1010	2040	2090	2160	
70	Z	112			272	
	L	950			748	
	F	1060			2035	

Table III shows that an increase in zinc butylxanthate results in a continuously increasing rate of vulcanization.

The mechanical properties lead to the conclusion that with over 4 per cent of zinc butylxanthate the rate of vulcanization is only slightly accelerated, while the quality of the films becomes considerably worse. Hence, from the standpoint of the quality, it is not advisable to add more than 4 per cent of zinc butylxanthate.

5. *Study of Different Proportions of p-Toluidine.*—Different proportions of *p*-toluidine were studied in the compounds of the following formulas:

	17	18	19	20	21	22	23
Smoked sheet	100	100	100	100	100	100	100
Sulfur	3	3	3	3	3	3	3
Zinc oxide	3	3	3	3	3	3	3
Zinc butylxanthate	3	3	3	3	3	3	3
p-Toluidine	0	0.5	1.0	1.5	2.0	2.5	3.0

The mechanical tests are summarized in Table IV.

A conclusion from Table IV is that a combination of zinc butylxanthate with *p*-toluidine has a tremendous advantage compared with zinc butylxanthate alone, both from the point of view of the rate of vulcanization and the mechanical strength.

An increased amount of *p*-toluidine (from 0.5 to 2 per cent) resulted in a continuous increase in the rate of vulcanization. While with 0.5 per cent (formula No. 18) the film vulcanized in 80 minutes, with 2 per cent the optimum of vulcanization was advanced by 40 minutes (formula 21), and the tensile strength increased from 231 to 266 kg. per sq. cm.

A comparison of the data for formulas 21, 22, and 23 shows that an increase of *p*-toluidine above 2 per cent is of no advantage; in amounts from 2 to 2.5 per cent a certain plateau or maximum value of mechanical properties was observed, and there was a reduction in the strength when the amount was increased to 3 per cent.

As a matter of fact, it is not practicable to add more than 2 per cent of *p*-toluidine in this formula.

TABLE IV

Curing Time in Min.	Test	No. of Formula 17	18	19	20	21	22	23
20	Z					241	249	230
	L					836	837	864
	F					2014	2085	1990
30	Z			195	219	258	263	245
	L			826	813	840	800	847
	F			1610	1780	2167	2105	2070
40	Z		213	206	243	266	268	
	L		740	828	790	850	806	
	F		1575	1705	1920	2261	2155	
50	Z		205	210	253	256	262	209
	L		740	817	850	850	823	800
	F		1515	1715	2150	2175	2155	1670
60	Z	145	207	229	253	257	252	
	L	774	747	828	865	859	834	
	F	1125	1545	1900	2199	2210	2105	
70	Z	140	229		256	244	243	
	L	797	769		815	843	814	
	F	1180	1705		2090	2060	1980	
80	Z	157	231			228		
	L	779	777			840		
	F	1225	1795			1915		
90	Z	160	239					
	L	808	757					
	F	1925	1810					

In conclusion, films of the following formulas were tested on the basis of data given in Tables III and IV.

	Formula 24	Formula 25
Rubber	100	100
Sulfur	3	3
Zinc oxide	3	3
Zinc butylxanthate	4	4
p-Toluidine	2	2.5

i. e., a study was made of the optimum proportions of zinc butylxanthate and *p*-toluidine, as discovered in the preceding tests.

The mechanical tests on these films are summarized in Table V, and a comparison is made with the results previously given for the films of formulas Nos. 15 and 21.

A conclusion may be drawn from Table V, that with 4 per cent of zinc butylxanthate the *p*-toluidine can be limited to 1.5 per cent, as any further increase did not add anything to the acceleration of vulcanization, or to the mechanical properties.

TABLE V

Curing Time in Min.	Test	No. of Formula 15	24	25	21
20	Z	242	296	167	241
	L	783	760	794	836
	F	1895	1565	1325	2014
30	Z	259	255	201	258
	L	744	756	720	340
	F	1930	1930	1450	2167
40	Z	268	265	239	266
	L	755	768	817	850
	F	2055	2040	1950	2261
50	Z	279	235	210	256
	L	772	769	807	850
	F	2150	1810	1695	2125

TABLE VI

	Tensile Strength Kg./Cm.² 1	Elong. at Break 2	Tensile Product 3 40′	Aging Co-efficient 4	Tensile Strength Kg./Cm.² 5	Elong. at Break 6 50′	Tensile Product 7	Aging Co-efficient 8	Tensile Strength Kg./Cm.² 9	Elong. at Break 10 60′	Tensile Product 11	Aging Co-efficient 12
1.0 per cent of *p*-toluidine. Formula 19												
Normal conditions	205	885	1815	..	209	867	1810	..	227	856	1940	..
5 days of aging	107	870	930	0.51	125	886	1085	0.60	146	884	1290	0.67
10 days of aging	35.4	758	267	0.15	125	780	975	0.54	106	828	877	0.45
1.0 per cent of *p*-toluidine, 1.0 per cent Age-rite. Formula 19a												
Normal conditions	196	875	1710	..	211	872	1840	..	222	867	1925	..
5 days of aging	161	868	1400	0.82	167	836	1400	0.76	158	818	1290	0.67
10 days of aging	185	833	1540	0.90	145	784	1135	0.62	133	760	1010	0.52
2.0 per cent of *p*-toluidine. Formula 21												
Normal conditions	251	829	2080	..	266	850	2261	..	256	855	2190	..
5 days of aging	248	811	2050	0.99	...	...	..	..	232	777	1800	0.82
10 days of aging	246	810	1920	0.96	223	830	1850	0.82	215	34	1790	0.82
2.0 per cent of *p*-toluidine, plus 1 per cent of Age-rite. Formula 821a												
Normal conditions	248	843	2050	..	237	819	1940	..	...	...	..	..
5 days of aging	215	815	1730	0.86	212	817	1730	0.89	...	...	..	..

It may be seen from the comparison of data for films of formulas 15 and 21 that they were almost identical in mechanical properties, but formula 21 had an advantage with respect to its rate of vulcanization.

6. *Study of Aging Resistance of Films Vulcanized with Zinc Butylxanthate and p-Toluidine, and Investigation of the Role of an Antioxidant (Age-rite).*—Films of the following formulas were tested for their resistance to aging

	19	19a	21	21a
Rubber	100	100	100	100
Sulfur	3	3	3	3
Zinc oxide	3	3	3	3
Zinc butylxanthate	3	3	3	3
p-Toluidine	1	1	2	2
Age-rite		1		1

Vulcanized films were subjected to accelerated aging in a Geer oven, at a temperature of 70° C., for five and 10 days. At the end of the period of aging the specimens were withdrawn from the oven, and after standing 24 hours their mechanical properties were investigated. A parallel test was made at the same time on similar specimens not subjected to accelerated aging.

The tests are given in the form of "aging coefficients" equal to the ratio F_1/F, where F_1 is the tensile product of the film after aging, and F is the tensile product of the film not subjected to aging.

The results of the tests are summarized in Table VI.

A comparison of the aging coefficients of the films of the formulas tested, showed that even compound No. 19, which resisted aging less than the rest, gives quite satisfactory aging coefficients. A comparison of formulas 19 and 21, showed that films with 2 per cent of *p*-toluidine have better aging resistance than films with 1% content; whence *p*-toluidine is an antioxidant in itself.

The addition of Age-rite to the compound with 1% of *p*-toluidine (formula 19a) increased the aging resistance of the film, whereas when the content of *p*-toluidine was 2 per cent (formula 21) the aging coefficient with or without Age-rite was almost identical.

Summarizing the tests of all the samples, we can draw the following general conclusions:

In order to achieve maximum acceleration of vulcanization with zinc butylxanthate, it is necessary to activate it with zinc oxide and *p*-toluidine. The optimum proportions are: 3 per cent of zinc oxide and 1.5 to 2 per cent of *p*-toluidine.

When choosing the amount of *p*-toluidine it is necessary to bear in mind also its correlation with zinc butylxanthate. If 4 per cent of zinc butylxanthate is considered the best proportion with 1.5 per cent of *p*-toluidine, it is sufficient to use 3 per cent of it with 2 per cent of *p*-toluidine. The last proportions, as already mentioned above, have the advantage over the first in their acceleration of vulcanization.

Furthermore, taking into consideration the beneficial influence of *p*-toluidine upon the aging resistance of vulcanized films, it is practicable to reduce the content of zinc butylxanthate in the formula at the expense of a larger amount of *p*-toluidine.

Thus, the ultimate formula of a cement is as follows:

Smoked sheet	100
Sulfur, precipitated	3
Zinc oxide	3
Zinc butylxanthate	3
p-Toluidine	2

PART II

TESTING THE CEMENT OF THE CHOSEN FORMULA IN CEMENTING SPECIMENS OF DUCK AND LEATHER WITH RUBBER

Cements of the following formulas Nos. 1 and 2 were tested for cementing leather and duck with rubber. Formula No. 1 is the first specimen of cement submitted by the Scientific Research Institute of Rubber Industry to the Industry, based on the combination of butylxanthate and *p*-toluidine.

	Formula No. 1	Formula No. 2
Rubber	100	100
Sulfur	3	3
Zinc oxide	5	3
Zinc butylxanthate	3	3
p-Toluidine	1	2

Cement, 5 per cent in solvent gasoline "Kalosha."

1. *Methods of Cement Preparation.*—Cement was made from rubber (smoked sheet), which to facilitate solution was first passed three times through closely adjusted mill rolls. The batch of rubber was placed in one-half the volume of solvent eventually to be used. After swelling for 24 hours the balance of the solvent was added, and the solution was agitated in a mechanical mixer for 12 to 15 hours until it attained absolute homogeneity. Then to reduce viscosity, 3 parts of methylated spirit to 100 parts of the cement (by weight) were added. To avoid prevulcanization, the other ingredients were added to the rubber solution 1 hour before its use. *p*-Toluidine, which dissolves well in gasoline, was added directly to the cement. The other ingredients were first moistened with gasoline, and then mixed with a small portion of the cement, and added to the main bulk in paste form.

2. *Technic of Cementing and Methods of Testing the Cemented Specimens.*—Black chrome-kid, duck, and soling pads, made in the laboratory of the Scientific Research Institute of the Rubber Industry, served as materials for cementing.

The surfaces of leather and rubber to be cemented received the following special treatments. The face of the leather was removed, and its surface buffed; the upper layer was removed from the surface of the rubber on a "Summit" buffing machine. No preliminary treatment was given to the duck. All materials were cut in standard sizes of 150 × 100 mm. Before applying cement, the treated surfaces of the specimens were washed with benzene.

Five grams of cement were applied in several daubs to each surface to be cemented.

The first coat of cement was rubbed in by a hard brush; the subsequent spreads were carefully distributed over the surface by a trowel. The number of spreads was determined on the basis of preliminary tests of different variants of spreading, *viz.*, three coats for leather, and four coats each for rubber and duck.

After the spread had dried, the respective specimens were brought together, slightly rolled over by a hand roll in order to eliminate air blisters, and put in a press for 15 minutes under pressure. Strips 150 × 20 mm. were cut from the central section of cemented specimens after pressing. The strength of the cemented joint was determined by separating these strips in a Schopper dynamometer, equipped with an automatic device for drawing the stress-strain diagram, from which the resistance of the tested specimen to separation, expressed in kg. per 1 cm. of the width of cemented surface was calculated. The average loads were computed on the basis of tests of 8 specimens.

3. *Testing of Cemented Specimens Kept in Different Conditions.*—In addition to determining the resistance to separation of specimens under normal conditions,

some were subjected to a number of special tests. These latter tests were developed by the Institute in collaboration with the laboratory of the factory "Proletarian Victory" No. 2, the object being to reflect to a certain extent the basic conditions to which the cement film would be subjected in the manufacture and use of footwear. These tests were as follows.

1. Specimens were separated after being kept for an hour at 20° to 25° C.
2. Thermal test No. 1. After being kept for one hour at 20° to 25° C., the specimens were placed in an air oven at 70° C. for 30 minutes, after which they were immediately separated while still hot.
3. Specimens were separated after being kept at 20° to 25° for one day, 5 days, and 10 days.
4. Specimens, which were kept for 5 days at 20° to 25° C., were placed in an air oven at 70° C., and after 30 minutes immediately separated while still hot.
5. Thermal test No. 2. The cemented specimens were kept for 5 days in natural storage, and then at 70° C. for three days, at the end of which they were separated while hot.
6. Hydro-thermal tests. Cemented specimens, after lying for 5 days at 20° to 25° C., were placed in an air oven at 70° C. for 12 hours. After every two hours of heating the specimens were moistened with water. After remaining 12 hours in the oven, the specimens rested for 12 hours at 20° C. to be placed again in the oven, this 24-hour cycle being repeated four times, after which their resistance to separation was measured.
7. Investigation of aging resistance.

After being kept for 24 hours at 20° C. the specimens were kept for 6 hours in an air oven at 70°, and separated after cooling.

8. The same test after keeping the specimens for 24 hours in the oven.
9. The same test after keeping the specimens for 72 hours in the oven.

The object of the tests Nos. 1 and 2 was to discover the capacity of the film to resist the operations of footwear manufacture, which follow immediately after cementing the sole. Tests Nos. 3 and 5 were made on specimens after they had remained for five days at room temperature, the object being to find out the capacity of vulcanized films to resist all possible extraneous influences. The results of tests of cements of formulas Nos. 1 and 2 for cementing specimens of leather plus rubber and duck plus rubber, are summarized in Table VII.

It is necessary to point out that, when considering the data of the table, comparisons should be made only of figures running vertically, as the tests of cements of formulas Nos. 1 and 2 were made on leathers from different lots, and the nonhomogeneity of the latter resulted in variations in the absolute values of the resistance to separation.

An additional column, "relative strength in per cent," was introduced to make possible a comparison of the horizontal figures of the table. As after five days' storing of specimens at a temperature of 20°, the cement films were vulcanized (judged by solubility test in gasoline), the values of the separation resistance of these specimens have been conventionally taken as units, and the results of tests on all other items have been figured as percentages of these values. In general, it was found from our observations that the methods of characterizing the cements on the basis of laboratory tests for separation of standard specimens (both under our method and that of the Central Scientific Research Institute of the Leather Industry) is only approximate, and fails to give a complete picture of the behavior of cement under certain conditions. This is particularly true of the cemented specimens of leather and rubber. This is the reason why an absolutely final judgment of the quality of cement can be made only on the basis of service tests.

TABLE VII

Conditions of Storing the Specimens before Separation	Cement Formula No. 1				Cement Formula No. 2			
	Leather and Rubber	Relative Strength in Per Cent	Duck and Rubber	Relative Strength in Per Cent	Leather and Rubber	Relative Strength in Per Cent	Duck and Rubber	Relative Strength in Per Cent
1. After keeping for one hour at a temperature of 20° C.	1.40	...	2.95	....	1.29	...	2.89	...
2. Thermal Test No. 1 for specimens after keeping for an hour at 20° C.	0.75	...	0.94	...	0.94	...	1.84	...
3. (a) After 1 day's storing at 20° C.	1.66	92	3.11	...	1.70	83	2.74	...
(b) After 5 days' storing at 20° C.	1.81	100	3.15	100	2.05	100	2.99	100
(c) After 10 days' storing at 20° C.	2.00	110	2.88	...	2.00	97.5	..	...
4. Thermal Test I for specimens, after 5 days' storing	1.22	67.4	2.40	76	1.60	78	2.01	67
5. Thermal Test No. 2	1.69	93	2.78	88	1.70	83	2.91	97
6. Hydro-thermal test	1.59	88	3.00	98	1.67	81	..	...
7. Study of aging resistance. Separation after 6 hrs. of heating in oven at a temperature of 70° C.	1.43	...	2.96	...	..	...	2.95	...
8. Same after 48 hours	1.60	...	2.83	...	1.84	...	2.82	...
9. Same after 72 hours	1.62	...	3.57	...	1.75	...	2.89	...

The table shows that the absolute values for separation in specimens of leather and rubber are lower than those for specimens of duck and rubber.

Bearing in mind that in the separation of leather and rubber, the tear is mostly observed on the leather side, the lower figures of separation in this case may be due to the comparatively poor strength of the leather used. As to duck, tear takes place either on the rubber side or in the film, the increased load thus being due to the strength of the rubber.

The following conclusions may be drawn from the data on the specimens cured (*i. e.*, allowed to set) in different conditions; those specimens have the least strength which are separated in a hot state after a thermal test, the maximum loss of strength being observed in specimens which were kept the minimum of time in storage.

By comparing the tests under items 3c, 5, and 6, it is found that the vulcanized cement film was sufficiently strong under the conditions, the loss of strength being on the average 10 to 20 per cent.

Separation resistance of the films after artificial aging confirms the previous conclusions about the good aging resistance of the films of the given formulas.

Storage at 20° C. for 1 to 10 days resulted in the case of cement of formula No. 1 in an increased resistance to separation, and in the case of cement of formula No. 2 in a resistance to separation of 5-day specimens showing no increase compared with a longer storing period.

A comparison of the data of "relative strength" shows that the differences in the behavior and strength of the films of these formulas, which were referred to in the section on the development of the formulas, did not appear in striking form under these conditions of test.

This fact once more confirms the low sensitivity of this method of testing.

PART III

THE STORING OF CEMENTS

The practical use of self-vulcanizing cements is handicapped by their property of rapid gelling, which is directly dependent upon the rate of vulcanization of the cement, and on the temperature at which it is stored.

The rapidity of gelling must be borne in mind, and in this connection the most favorable conditions and periods of storing the cements should be chosen.

Under production conditions, to avoid the deterioration of cement, it is manufactured in small quantities, which are expected to be consumed immediately, or the cements are made in two solutions: one with sulfur, and another with accelerators, the solutions being mixed in suitable proportions before using. By this method, each of the component parts can be prepared and stored for a long period of time without any risk of gelling.

An observation was made of the change of viscosity of stored cements, with the purpose of discovering the possible time and methods of storing cements, of the formulas proposed:

No. 1.—Five per cent cement prepared from unmilled rubber in gasoline (3 per cent of methylated spirit being added) with the formula:

FORMULA OF THE CEMENT NO. 1

Rubber (smoked sheet)	100 parts by weight
Sulfur	3 parts by weight
Zinc oxide	5 parts by weight
Zinc butylxanthate	3 parts by weight
p-Toluidine	1 part by weight

No. 2.—Of the same cement, prepared in two parts:

	a	b
Smoked sheet	100 parts	100 parts
Zinc oxide	5 parts	5 parts
Sulfur	6 parts	
Zinc butylxanthate		6 parts
p-Toluidine	1 part	1 part

No. 3.—Five per cent cement from unmilled rubber, in gasoline (3 per cent of methylated spirit being added) under formula No. 2, prepared in two parts, of two types:

	Type I		Type II	
	c Parts	d Parts	e Parts	f Parts
Rubber (smoked sheet)	100	100	100	100
Sulfur	6		6	
Zinc oxide	3	3	3	3
Zinc butylxanthate		6		6
p-Toluidine		4	2	2

All cements were kept under the same conditions in the dark at 20° C. The viscosities were measured periodically with a Stormer viscometer.

The results are summarized in Table VIII.

TABLE VIII

VISCOSITIES IN SECONDS PER 100 REVOLUTIONS

Type of Cement	Period of Storing of Cements						
	1 Hour	3 Hours	6 Hours	12 Hours	24 Hours	48 Hours	5 Days
Mixed cement formula No. 1	405	470	606	804	25,420	gell	
a	409	370	365	382	387	391	
b		356	355	369	460	405	
c	500			495			686
d	420			700			1412
e and f	A slight increase in viscosity of cement after one month's storing						

The table shows that it is dangerous to keep mixed cement more than 6 hours, as a noticeable increase of its viscosity results in that period. After 24 hours' storage the cement is no good for use.

It is quite safe to keep cements in two parts, "a" and "b" during the time checked (2 days).

In the case of a more rapidly vulcanizing cement (formula No. 2), even when prepared in two parts, as shown by the table, a correct distribution of ingredients in the parts of the cement must be borne in mind. Thus, when cement is stored in two parts, "c" and "d," it is observed that while the viscosity of part "c" remains unchanged after 12 hours of storing, increasing slightly after 5 days of storing, the same is not true of part "d." In checking the homogeneity of this part, clots of vulcanized cement were discovered. Bearing in mind that formula "d" contains no sulfur, only one possible assumption can be made, that vulcanization took place under the influence of zinc butylxanthate and *p*-toluidine. This is confirmed by previous observations that when zinc butylxanthate and *p*-toluidine are mixed together in powder form, an energetic reaction takes place between them.

It is supposed that at a certain concentration of zinc butylxanthate and *p*-toluidine, as a result of a similar reaction in the cement, sulfur is liberated in a state active for vulcanization.

No such phenomenon is observed after changing the ratio of zinc butylxanthate and *p*-toluidine as in the formulas "e" and "f," and the cement in this case can be safely stored for a long time.

On the basis of the above, a deduction can be drawn that the most practical way of storing cement of formula No. 2 is by preparing it in the form of two separate cements "e" and "f."

Cementing Capacity of Cements Stored for a Long Time

To check the cementing capacity of solutions after storing, the following cements were tested:

1. Cement of formula No. 2, prepared in two parts, was stored for 12 hours, after which both parts were mixed. Leather and rubber were covered with cement immediately after the latter was mixed.
2. Each part of cement formula No. 2 was stored for 5 days, after which the parts were mixed together, and application was made in the same manner as in case No. 1.

The resistances to separation for these various cements are summarized in Table IX.

TABLE IX

Period of Storing the Specimens under 20° C.	Resistance to Separation in Kg. per Cm. I Variant	II Variant
1 day	1.33	1.45
5 days	1.47	1.45
10 days	1.67	

On the basis of these results, we can conclude that storing of cement of formula No. 2 for 5 days in the form of two separate solutions had practically no effect upon its cementing capacity.

As a general conclusion we would recommend for practical use a self-vulcanizing cement of the following composition:

Smoked sheet	100 parts by weight
Sulfur (precipitated)	3 parts by weight
Zinc oxide	3 parts by weight
Zinc butylxanthate	3 parts by weight
p-Toluidine	2 parts by weight

The cement is made of unplasticized rubber dissolved in benzene.

The cements are stored as two separate solutions A and B of the following composition:

	A	B
Smoked sheet	100	100
Sulfur	6	
Zinc oxide	3	3
Zinc butylxanthate		6
p-Toluidine	2	2

Self-vulcanizing cement of the composition mentioned is already used in practice, both by the rubber and other industries.

In the rubber industry it is used in different shop operations for cementing vul-

canized details, repairing, etc. As a concrete example, we might mention the cementing of transmission belts or the repairing of automobile tubes.

As to other branches of the industry, we will point out the use of self-vulcanizing cement in the leather and footwear industry for cementing rubber soles to the uppers. The Leningrad factory "Proletarian Victory" No. 2 after extensive industrial tests which gave very favorable results, introduced self-vulcanizing cements for work in one of its slipper manufacturing shops.

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Crystals and Fused Substance in Stretched Rubber

(A Preliminary Communication)

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When rubber is stretched, the arrangement of the molecules in the space lattice does not come to an end when the elongation is terminated, but continues for a certain time afterward. The final state of orientation for any elongation depends upon the temperature in the sense that within a wide temperature range there is at each temperature a definite ratio between the quantity of crystallized substance and the glass-like fused component.

Within this temperature range, the proportion of crystallized substance diminishes with increase in temperature. This change is reversible, and the equilibrium is greatly influenced by the pressure.

It may be considered as an established fact today that natural rubber is essentially a mixture of various polymers of an unsaturated hydrocarbon.[1] At ordinary temperatures and in the absence of mechanical stress, it is an isotropic glass, both in the raw and vulcanized states. When deformed mechanically, particularly when stretched, it becomes anisotropic, a change which is evidenced by the appearance of an optical double refraction[2] and an x-ray fiber diagram.[3] This phenomenon is attributable to an orientation of the molecules in the direction of stretching and their arrangement into a space lattice which can be measured and defined accurately.[4] The increase in double refraction as well as the clearness of the reflection interference pattern in the Roentgen diagram is proportional to the degree of elongation of both raw and vulcanized rubber,[5] and it is reversible after a certain time of relaxation. In natural rubber, the reversibility of the phenomenon is disturbed by flow phenomena, which upon prolonged mechanical stress lead to permanent deformation. In well vulcanized rubber these phenomena are of little significance over a wide range of temperatures.

Judged by previous experiments, the orientation phenomena appear to come to an end with the termination of stretching, or at least a very short time afterward.[6] As a matter of fact, however, in vulcanized rubber stretched to 400 per cent or more at room temp., the orientation increases considerably for several minutes after termination of the stretching, and then slowly approaches a final state after many hours.[7]

The change in the orientation was measured at constant temperature by following the change in the double refraction of monochromatic light (sodium-vapor lamp) by means of a sensitive Babinet compensator with mechanical recording of standardizations. In the x-ray diagram, the development of the lattice orientation could be followed by a series of diagrams at successive short intervals of time showing an increase in the intensity and sharpness of the reflections (whose positions remained otherwise unchanged) at the expense of the diffuse background fogging of the film.

The change in the anisotropy after termination of the stretching, which may be

termed "spontaneous orientation," was determined after various final effects of preliminary elongations ("prestrains") at various temperatures. The extent of the spontaneous orientation increased with the magnitude of the preliminary stretching, and diminished with the temperature. The rate at which spontaneous arrangement took place increased with the magnitude of the "prestrain" and with the temperature.

These phenomena are to be attributed to a spontaneous crystallization of the fused substance, and this crystallization is strongly influenced by pressure.

In view of these facts, an attempt was made, by following the course of the fusion, to decide whether the crystallized substance is homogeneous or contains different components.

The change in the optical double refraction at a constant elongation with change in the temperature was determined for rubber which had crystallized to its final state of orientation after stretching to more than 400 per cent at 20° C. An increase of temperature resulted in a lessening of the double refraction, which then remained constant at the particular temperature. By lowering the temperature it was proved that the change is reversible.

In the x-ray diagram, the diffused background fogging of the film corresponding to the diminution in the double refraction increased at the expense of the intensity of the reflections, which retained their relative positions except for changes in distance brought about by differences in temperature.

According to these results, there is, within a wide temperature range (a range of 40° was measured), a definite equilibrium of the crystallized substance and amorphous fused component corresponding to each temperature.[8] As a consequence, the stretched rubber must contain crystallites of different melting points, and therefore different components. The crystalline phase changes its composition with the temperature.[9]

An obvious conclusion from this is the fact that during crystallization the individually similar polymerized products tend to unite (formation of micelles). Between the crystals which contain solely or to a great extent the most highly polymerized molecules, and those which contain solely or preponderantly the lowest polymers, there are as many intermediate stages as there are stages in the polymerization. This lends support to the idea that the different components give a series of mixed crystals. Upon stretching rubber at a constant temperature, mixed crystals[10] containing a maximum proportion of the highest polymerized component are first formed, and on heating, the crystals containing the greatest proportion of the smallest molecules melt first.

The way in which the double refraction depends upon the elongation and upon the temperature, with the results described above, and the concordant fusion curves of natural rubber obtained by von Susich,[11] all lead to the conclusion that the fusion point of crystalline rubber depends greatly upon the pressure, *viz.*, increases with increase in pressure (degree of elongation). In agreement with this is the increase in density which takes place when rubber is stretched, as well as the relatively slight heat of crystallization.

In conclusion, then, stretched rubber consists of a polyphase system, in which within a wide range of temperatures, crystals and fused substances of varying compositions are in an equilibrium which depends greatly upon the pressure. It is on this basis that the characteristic properties of rubber, particularly its wide range of elasticity, can be readily explained.[12] Furthermore, in connection with future investigations of rubber, the way is opened to a method of attack which is based on the phase rule and has been verified for heterogeneous systems.

References

[1] C. O. Weber, *Ber.*, **33**, 779 (1909); Caspari, *J. Soc. Chem. Ind.*, **32**, 1041 (1913); Feuchter, *Kolloidchem. Beihefte*, **20**, 434 (1925); Pummerer and Koch, *Ann.*, **438**, 294 (1924); Pummerer and Pahl, *Ber.*, **60**, 2152 (1927); Ostwald, *Kolloid-Z.*, **40**, 58 (1926).

[2] Bjerkén, *Ann. Physik*, **43**, 808, 818 (1891); Rossi, *Beibl. Ann. Physik*, **35**, 206, 264 (1911); **36**, 67 (1912); Kröger, *Kolloid-Z.*, **45**, 46 (1928); Zocher, *Kautschuk*, **8**, 173 (1929); Geel and Eymers, *Z. physik. Chem.*, **3**, 240 (1929).

[3] Katz, *Naturwissenschaften*, **13**, 411 (1925); Meyer, Ferni, and Hohenemser, *Kautschuk*, **11**, 92 (1935).

[4] Mark and von Susich, *Kolloid-Z.*, **46**, 11 (1928).

[5] Double refraction: Zocher, *loc. cit.;* Geel and Eymers, *loc. cit.* Roentgen diagrams: Hauser and Mark, *Kolloidchem. Beihefte*, **22**, 63 (1926); *Kolloid-Z. Ambronn-Festschrift*, **1926**, 64.

[6] Acken, Singer, and Davey, *Ind. Eng. Chem.*, **24**, 54 (1932); Long, Singer, and Davey, *Ind. Eng. Chem.*, **26**, 543 (1934).

[7] For preliminary experiments see Wittstadt, Dissertation Göttingen, **1933**.

[8] In addition to the quantitative determination of the double refraction, a photometric measurement of the change in the intensity of the diffused blackening and of the reflections as functions of the temperature should throw light on the relative quantities of crystals and fused substances.

[9] The fact that the arrangement of the reflections in the x-ray diagram is retained with change in temperature is not at variance with this conclusion; for the elementary cell of the space lattice in rubber results from periodically recurring parts of the molecule.

[10] The fusion of natural rubber obtained by von Susich (*Naturwissenschaften*, **18**, 915 (1930)), which shows the way in which the elongation depends upon the temperature, whereby a phase diagram appears, gives accordingly the fusion point of the crystals with the highest melting point and with the highest proportion of highly polymerized components.

[11] von Susich, *Naturwissenschaften*, **18**, 915 (1930); Sauter, *Z. physik. Chem.*, **21B**, 161 (1933).

[12] Staudinger and Leupold, *Ber.*, **67**, 304 (1934). The kinetic theory of rubber, as developed by Meyer, von Susich and Valko (*Kolloid-Z.*, **59**, 208 (1932)) and Meyer, Ferni, and Hohenemser (*Kautschuk*, **11**, 88 (1935)) remains applicable in its fundamentals even in the face of the new theories (cf. Sauter, *loc. cit.*).

[13] A detailed description of the results in the present communication will be published later in the same journal.

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Plasticity and Elasticity, with Special Reference to Unvulcanized Rubber

J. Hoekstra

When working in the field of elastic and plastic properties of plastic materials such as unvulcanized rubber, one is confronted with the fact that there is very little reliable knowledge in that field. Some time ago Prof. J. M. Burgers,[1] in an address before the Foundation of Biophysics, gave a fundamental and extended explanation of the theory of plasticity and its relation to elasticity. Previous to experimental investigations of plasticity, elastic-plastic behavior was assumed to be so simple that it could be reproduced by means of a system of steel springs and pistons of constant friction. It was thus clearly a problem of hydrodynamics and mechanics. Up to the present time, the mechanical properties of highly polymerized substances have remained a mystery to research workers. In an investigation of polymers of high molecular weight, Meyer, Susich, and Valko[2] proposed that the elasticity of these substances depends on the transverse motion of the long molecules, and is thus closely analogous to the elasticity of gases. Their strong argument in favor of this is the fact that the elasticity of rubber, for example, has a positive temperature coefficient, which is in agreement thermodynamically with their suppositions. It is now known from the great difference between the mechanism of the elasticity of rubber and of metals, and also from the stress-strain diagram of rubber (the well-known S-curve), that it is very improbable that the properties expressed by means of pistons and springs can be correctly applied to a substance like rubber. The same holds true for other highly polymerized substances. In spite of the foregoing, it is not surprising that the measurements of Scott,[3] of Peek,[4] and of Houwink[5] showed close agreement with the theory, at least in a great number of fields of flow which were investigated. The agreement always holds true for relatively large shearing forces, *viz.*, when the shearing forces are great compared with the intramolecular or thermodynamic forces. When the latter forces cease to operate, there appears a flow which is generally known as viscous flow. For smaller shearing forces, however, the change in shape and the plastic flow are not measurable by the methods applied by the above-named authors.

However, in the field of still smaller shearing forces there appears for elastic-plastic materials a very complicated system of elasticity-with-relaxation in which the plastic flow is perhaps still present, but may be neglected. In the field to which the elasticity, the relaxation, the elastic after-effect, and the hysteresis in a stress-strain diagram of rubber and of many fibrous materials belong, theoretical and experimental work fails to explain the quasi-elastic behavior. This field, in which there is no actual change of form and in which no true flow takes place, must no longer be considered as purely plastic, and must therefore be held for further investigation.

Between the field of viscous or quasi-viscous flow and that of "special" elasticity which is exhibited by substances of high molecular weight, there lies the field, extremely interesting technically as well as scientifically, in which viscosity and elas-

ticity both play an important part and are very closely interrelated. Our knowledge of this field is very small in spite of the important work of the above-named investigators. The reasons for this lack of reliable knowledge will be discussed later.

In analyzing the mechanical behavior of an elastic-plastic material, we generally try in the first place to draw a distinction between that part of the deformation which remains after removal of the deforming forces and that part of the deformation which disappears of its own accord; *viz.*, between the plastic and the elastic or quasi-elastic deformations. If it were possible to study all the elastic and plastic deformations by some standard method, there would immediately be the additional problem of a plasticity suitable for basic comparisons of different materials, and the application of this comparison to different kinds of deformation.

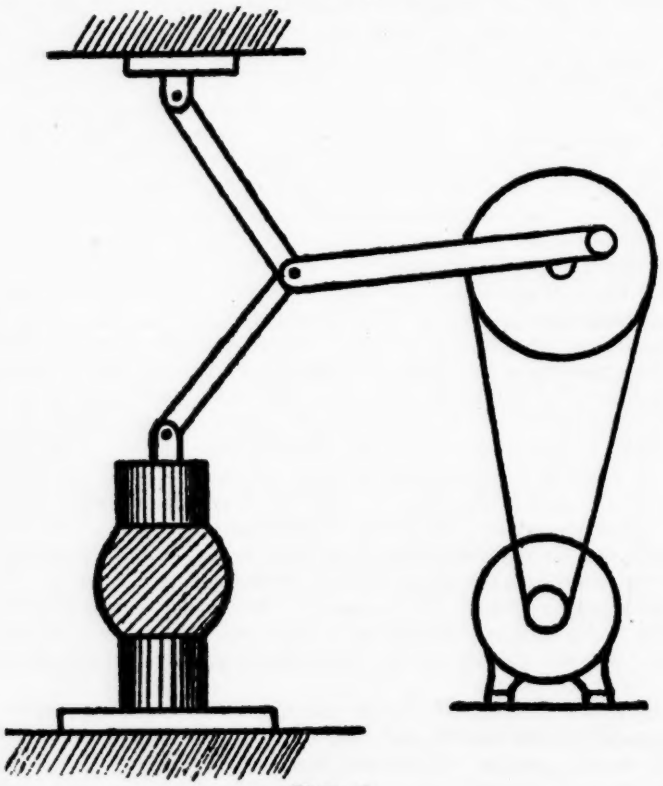

Figure 1

In the following I shall first show the possibility of a distinction between plastic and elastic deformations, discuss briefly a suitable study of plasticity, and then indicate in conclusion the most suitable direction for future investigations.

The importance of distinguishing the mechanical behavior of highly polymerized substances into elastic and plastic parts is shown by the following example taken from the scientific literature. In an investigation by Stamberger[6] it is reported that plasticized rubber which holds its plasticity (softness) almost unchanged for an

unlimited time will not retain its plasticity if mixed with carbon black. Such mixtures acquire considerable stiffness within a day or so after mixing.

It is probable that the increase in stiffness depends upon the formation of a structure between, or the relative position of, the rubber molecules or micelles and the particles of carbon black. Thus it influences the elastic elements of the rubber and increases its elasticity. Not only a lack of knowledge of the properties of the elastic-plastic state, but above all the inability to differentiate between the elastic and plastic components of changes in form, prevent at the present time a solution to this question.

Not only in the case of research of the type mentioned above, which is chemical in nature, but also in the case of purely technical and mechanico-physical investigations, an inaccurate differentiation between the elastic and plastic components of a system frequently lead to confusion and false conclusions.

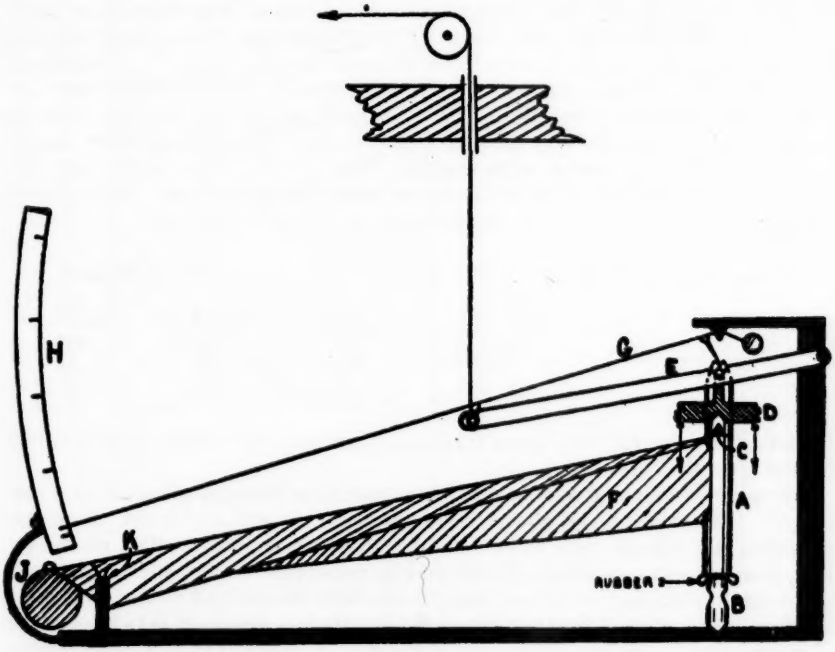

Figure 2

For rubber investigations and also for manufacturing control the so-called "recovery" after stretch is frequently measured. Here the material is compressed for a fixed time with a fixed force (or the speed of deformation may be measured). Figure 1 shows the principle of a plastometer which is somewhat similar to that of Karrer.[7] An eccentric driven by a synchronous motor pushes down a plunger by means of a lever system, causing the sample to be compressed. The plunger is then raised, leaving the material free again. A *gage* for the measurement of thickness remains in contact with the sample, and in this way the recovery is determined. Measuring the speed of deformation instead of the force gives a better idea as to what actually happens in most material-deforming machines.

The balance plastometer[8] is an example of an apparatus which is suitable for the measurement of recovery after compression by a constant force. It was designed by and is used by the Netherlands Government Rubber Institute at Delft. Here a rubber sample is compressed between two plungers A and B (see Fig. 2) by a weight, not shown in the figure, which is fastened on the cross-beam D. The force of the weight is brought down on knife C, which is fastened to the plunger A. By means of lever E, the weight bearing the cross-beam D is removed from knife C. When this weight is removed, the balance F is in equilibrium with a plunger A and a counterweight J, with the center of rotation at K. Independently, whether or not the load is applied, the thickness of the specimen can be measured at any moment by means of a pointer G on a scale H.

A set of values from the literature is given here for illustration. It concerns the influence of benzidine on the elasticity of unvulcanized rubber. Samples of plasticized rubber compounded with different proportions of benzidine were compressed for three minutes in the same plastometer. The thicknesses attained (in millimeters) were called the "flow numbers." The samples were then quickly removed from the apparatus, and after an interval of one minute the thicknesses were again measured. The increases in thickness (in millimeters) were called the "recovery" values. The "recovery" should, however, be expressed as the quotient of the increase in thickness on recovery divided by the thickness attained from the compression; it is thus expressed as a percentage. This is called the "percentage elasticity," and is included in the table below, which is taken from the *Vanderbilt News*:[9]

INFLUENCE OF BENZIDINE ON THE ELASTICITY AND PLASTICITY OF RUBBER

	Without Benzidine	1/16 % Benzidine	1/8 % Benzidine	1/4 % Benzidine
Flow number (mm.)	364	434	454	445
Recovery (mm.)	14	30	48	32
Elasticity (%)	4	7	10	7

The effect, which seems very great according to the recovery values, becomes much smaller after the correction is made.

Yet with a certain correction there is no "difference between plasticity and elasticity." The values given above for the recovery as well as for the percentage elasticity, run parallel with those for the softness (technically called plasticity). This, however, is no accident. Karrer and his associates[10] have made a great number of determinations which show that the elasticity determined by their method is practically a function of the plasticity. Such a relation, however, is to be expected after consideration of the method used, and must not be regarded as a true property. The reason is that compression takes place during a fixed time. In this method it is assumed that there is a definite relationship to most material-deforming machines, such as calenders and extruding machines, in which the material is worked for a definite length of time. Ordinarily it is desired to obtain the recovery of a substance after it has been subjected to such technical treatment. With compression for a fixed time it becomes impossible to differentiate between plasticity and elasticity. In a given time a softer material is compressed much more than is the stiffer one, and consequently shows less return. This difficulty can be overcome simply by compressing at a fixed rate of speed instead of during a fixed time. The trouble in distinguishing between plasticity and elasticity is none other than the relaxation, which is the spontaneous disappearance of the stresses initially introduced into an elastic-plastic material. The weaker the material is, the greater

in magnitude is this phenomenon, and the sooner it disappears. This relation may not hold true in a comparison of different materials. In general, however, and certainly for substances such as unvulcanized rubber, the relaxation increases with increase in plasticity. Whenever compression is maintained for a given time and the load then removed, the deformation at the beginning decreases much faster in the case of a softer substance than it does in the case of a stiffer one. The differences in recovery between a soft and a stiff material of the same kind are thus attributable to their differences in plasticity.

It is now necessary to find a method in which measurements can be made which reduce to a minimum the difficulty caused by relaxation. This method, in which I have made use of a balance plastometer, depends upon the following facts.

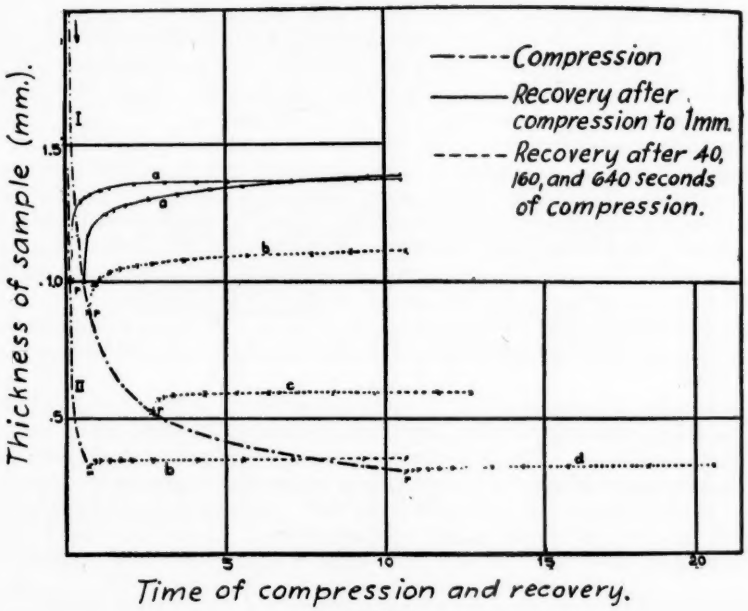

Figure 3

The speed of relaxation, *i. e.*, the speed at which deformation disappears, is to a great extent dependent on the softness of the material. Let it now be assumed for a first rough approximation that this speed is inversely proportional to the time necessary to compress the specimen to a certain thickness by a fixed load (not inversely proportional to what is generally called plasticity, *e. g.*, the thickness which the specimen reaches after a certain time of compression). It is not possible to put this supposition into exact form, but it is reasonable to suppose that it is possible for the internal forces to disappear in the one case equally as fast as the external forces in the other, with the same material and the same sample.

On the basis of this presupposition, we now come to a simple method of measurement which does not depend on the elasticity itself, but on a quantity which in the first place depends on the elasticity. The compression must therefore be *to a fixed thickness* (not for a fixed time), after which the load is removed and the path of recovery followed. If the supposition is correct, the relaxation is in both cases given

an equal opportunity. The soft material is compressed faster, and the greater relaxation takes place over a shorter period of time. With a harder material the reverse is true.

The statements previously made are demonstrated by the measurements plotted in Fig. 3. Here Curves I and II represent the compressions of two samples of rubber, in the balance plastometer, one of which was plasticized a very short time and the other a very long time. In each the compression was interrupted at point r, and the recovery followed. Curve I with its four side branches, a, b, c, and d, represents four recovery measurements on the harder material, and Curve II with its two side branches, a and b, measurements of the softer. If, now, the recovery in the harder material is compared after several compressions, it is evident that as the compression is continued, the recovery decreases rapidly. Moreover, if the recovery of the harder material is compared with that of the softer, both after 40 seconds compression, the softer appears to possess a much lower elasticity (Curves Ib and IIb). The results are very different, however, if both materials are compressed to 1 millimeter instead of compressing both for a given time. From Ia and IIa it is evident that the recovery is very much the same.

Naturally the experiments must be controlled so that the change of form and not the elasticity is actually measured. This change of form is a direct result of the elastic stretch applied. Since the recovery, however, is a very slow process (slower in proportion to the hardness of the material, at least for unvulcanized rubber), relaxation also takes place during recovery. Furthermore, the shorter time for the faster recovery gives less chance for relaxation, so that a measure of the elasticity is obtained.

Thus it is evident that there is an opportunity of a satisfactory differentiation between the two kinds of deformation. However, a really exact difference has not been found.

At this point the true plasticity (from the phenomena of flow and yield value), must be taken into consideration, with first thought to its relationship with that previously mentioned. Plastic materials are always judged by their yield value, and a measurement of the yield value gives a means of determining whether or not the mechanical behavior of a material is plastic.[11] As long as the yield value is not reached, deformation is only elastic or quasi-elastic. In the following equations for plastic flow, the yield value will be designated as f. Now from experiment the relationship is known between the shearing force τ and the speed of stretch $\frac{dv}{dx} = D$ (see Fig. 4), which offers a means of comparison. The limit to which the deformation can be made before plastic flow begins is then measured, that is, the deformation for maximum elastic stretch. Thus it is possible to determine the elasticity, and to subtract this elastic deformation from the total deformation, by means of which the difference between elasticity and plasticity is obtained. This method is not at all simple, since one usually has to deal with quasi-elasticity, in which a time factor enters. Actually the method can never be applied, since it is obviously impossible from experimentally measured forces and deformations (or speeds of deformation) to determine the relationship between τ and D. It becomes necessary then to resort to a fixed basic comparison, to classify the deformation as a definite type, and to compare the results with those obtained from an apparatus in which this type of deformation is more or less standardized. An example may explain the process and its difficulties.

Let us consider the seemingly simple process of compression between two parallel plates by a constant load. According to Scott (and independently from the results

of Peek) the flow is mathematically analyzed by application of certain hypothetical equations, with approximations which are not entirely true. The relatively simple formula of Bingham:

$$D = \mu(\tau - f)$$

in which τ is the shearing force (see Fig. 4, the left-hand side), D the rate of shear $\frac{dv}{dx}$, μ the mobility, and f the yield value, also gives an unsatisfactory comparison. The matter becomes still worse if the controversy of Peek and Scott is examined, from which it is evident that a difficult situation arises in drawing a distinct boundary between that part of the deformation which is elastic and that which is plastic, When a sample is deformed by compression between parallel plates to different thicknesses, there must be totally different values of τ, and in consequence the parts of the specimen bordering on the compression plates are elastically deformed and do not flow. A situation then appears such as is sketched in Fig. 1. The difficulty in the above-named controversy is a fundamental one. On the whole we do not need to follow the mathematical considerations of the above-named authors, and we can restrict ourselves to the fundamental formulas. This holds true for the yield

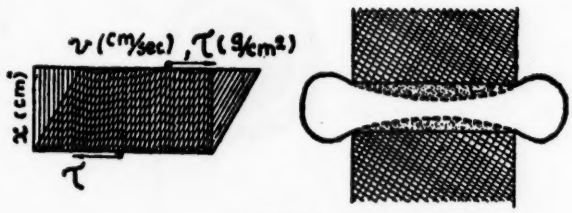

Figure 4

value f. On the one hand, this f causes considerable complication in the comparison given by the formula; but, on the other hand, it is a factor which can be neglected for somewhat greater deformations, especially when using the formula for quasi-viscous flow according to Waele:

$$D = \mu' \tau^n \quad \text{or}$$

$$\tau = \eta' D^{\frac{1}{n}}$$

Thus it becomes impossible to calculate the relationship between τ and D from these formulas and the experimental data. We must still write the general relationship:

$$D = \mu(\tau - f(D, t))$$

and the form of the function f must then require further experimental work.

The above statements seem to give the idea that knowledge of the mechanical behavior of high polymers is very small. Indeed, it is the opinion of the writer that this knowledge is actually still less. It has been the purpose to show that the great difficulty in the investigation of highly polymerized plastic substances is not of a mechanical but of a physical-chemical nature. It is extremely difficult if not impossible to make a choice between these different equations.

Naturally it cannot be denied that plastometers in general at the present time, especially those with parallel plates, are technically of the greatest importance. Nevertheless for the solution of the questions brought up here for discussion, the calculation of the properties involved in compound flow, because of its difficulty

and uncertainty, is a difficult problem which can be overcome only with a new technic. There are many difficulties which one must overcome when making observations on the mechanical behavior of elastic-plastic materials if he wishes to deform a specimen in such a way that D and τ are alike at each point in the material, for then plastic flow and elastic deformation can no longer take place at different points at the same time. Furthermore, variable deformation and variable relaxation at different points of the same sample can no longer cause a twisting in the flowing form. Knowing the empirical relation which the behavior of flow has on elastic-plastic substances, we can differentiate non-permanent (elastic or quasi-elastic) deformation from plastic flow. Thus we come to a real difference between plasticity and elasticity.

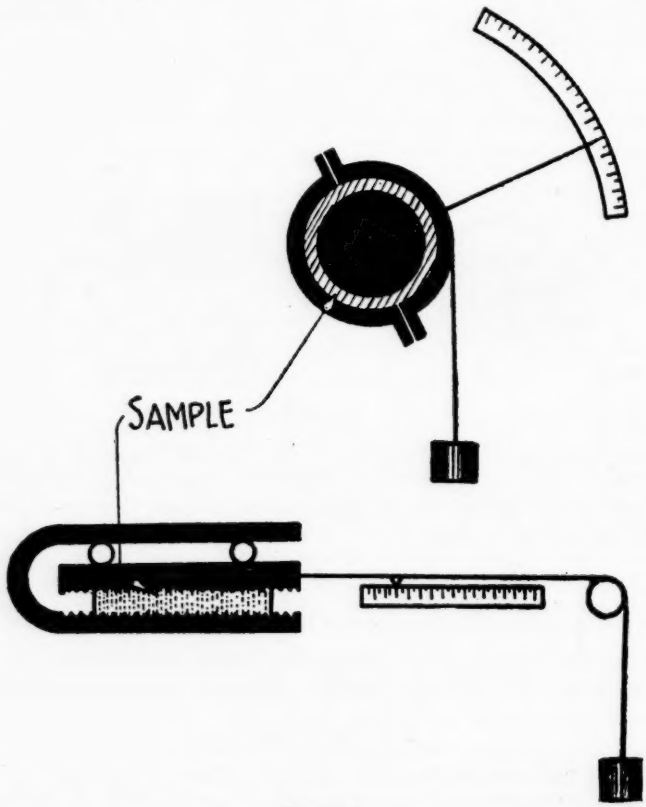

Figure 5

Figure 5 is an illustration of instruments constructed for these purposes. In the one instrument the specimen has the from of a ring; in the other it is a plate. Whereas in the first case D and τ are not perfectly alike at each point of the deformed sample, in the second case all the shearing is measured, which is small with respect to the length of the plate. By the addition and removal of weights one can investigate by means of these instruments the plastic flow, the elastic deformation, and the relaxation of all such materials which can be more or less deformed. Naturally, in

using this apparatus, certain precautions must be taken into consideration. For example, one must be certain that before beginning the measurements the specimen must again have completely lost its internal strain which it had originally acquired in the apparatus, as by warming. One must also be certain that no slipping takes place.

No difficulties seem therefore to stand in the way of broadening our knowledge of the mechanical behavior of high polymers.

References

[1] Burgers, *Nederl. Tijdschr. Natuurkunde*, **1**, 209 (1934).

[2] Meyer, Susich, and Valko, *Kolloid Z.*, **59**, 208 (1932).

[3] Scott, *Trans. Inst. Rubber Ind.*, **7**, 169 (1931–32).

[4] Peek, *J. Rheology*, **3**, 345 (1932).

[5] Houwink, "Physikalische Eigenschaften u. Feinbau v. Natur u. Kunstharzen," Leipzig, Akad. Verl. Ges., **1934**.

[6] Stamberger, *Kautschuk*, **7**, 182 (1931).

[7] Karrer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 158 (1929); RUBBER CHEM. AND TECH., **2**, 601 (1929).

[8] Hoekstra, *Physics*, **4**, 285 (1933); *Kautschuk*, **9**, (1933); RUBBER CHEM. AND TECH., **7**, 136 (1934).

[9] Anon., *Vanderbilt News*, **1**, 11 (1931).

[10] Karrer, Davies, and Dieterich, *Ind. Eng. Chem. Anal. Ed.*, **2**, 96 (1930); RUBBER CHEM. AND TECH., **3**, 295 (1930).

[11] At a meeting of the Section on Industrial Chemistry, on a day devoted to plasticity, Dr. R. Houwink made a statement that it is better not to speak of substances as being plastic, but to give the term "plastic" to the behavior of certain materials under certain circumstances. So it may be that what we regard here as plastic behavior will later, when more exact considerations of the details are known, be termed quasi-viscous or quasi-elastic.

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Thixotropy and Plasticity in the Rubber Industry

H. Freundlich

Sols and gels are characteristic colloidal systems. In sols the continuous phase or dispersion medium is a liquid and is in excess; the disperse phase is distributed in this medium in the form of small particles invisible in the ordinary microscope, and having diameters below 0.5 μ. The particles may be liquid or solid or have a more complicated structure. The term colloidal may be used in a somewhat broader sense, to include for instance, latex which contains a certain percentage of larger particles visible in an ordinary microscope, and with diameters up to about 5 μ. It is arbitrary to draw the line of demarcation between colloidal and non-colloidal systems at 0.5 μ; most properties of colloidal systems may be found in systems containing larger particles (up to about 6–7 μ), and most methods used in colloid science may be applied to them.

The term gel is not so easy to define. The conception favored in the earlier days of colloid chemistry that gels are the counterpart to sols, having a solid medium of dispersion and a disperse phase consisting of small drops of liquid, is not now popular and does not seem probable. It is assumed by many investigators that gels have a structure similar to that of foams or concentrated emulsions, the disperse phase consisting of small solid particles and the dispersion medium being liquid as in the case of sols; but it is present in very thin layers, generally only a few mμ thick, separating the solid particles from each other.

Nature of Thixotropy. Thixotropy and Plasticity

That sols and gels may be mutually transformed is a common experience. The non-isothermal, reversible sol-gel-transformation is well known: an aqueous concentrated solution of gelatin heated over 40° is a sol; it turns to a gel when cooled down, becoming a sol again on heating, and this process may be repeated at will, provided that the gelatin is not hydrolyzed by heating up to too high temperatures. Yet it was not noticed until a few years ago that an isothermal, reversible sol-gel-transformation is likewise a frequent colloidal phenomenon (Szegvari and Schalek, *Kolloid Z.*, **32**, 318; **33**, 326 (1923)): a gel may be liquefied to a sol simply by shaking or stirring, and the sol solidifies to a gel again when left to itself, a process which also may be repeated at will. The term "thixotropy" (Péterfi, *Arch. Entwicklungsmech.*, **112**, 660 (1927)) embraces this isothermal, reversible sol-gel-transformation.

It seems justifiable to apply this term to some closely related phenomena. On the one hand it is not necessary that the particles of the disperse system shall be of colloidal size; systems with much larger particles (with diameters up to 1 μ and more), such as clay and powdered slates, may show strong thixotropic effects when mixed with suitable amounts of water or aqueous solutions. On the other hand, concentrated sols may show changes in their viscosity, owing to causes similar to those instrumental in causing the thixotropy of gels; their viscosity may decrease greatly on shaking and increase again to the original value when the sol is left to itself.

A few characteristic cases may be given as examples. Concentrated aqueous sols of the basic oxygen compounds of iron, aluminum, etc., become thixotropic if small amounts of coagulating electrolytes be added; the thixotropic state may be considered as the first step towards coagulation (Freundlich and Söllner, *Kolloid Z.*, **44,** 309; **45,** 348 (1928)). Finely powdered or highly dispersed minerals such as clays, bentonite, and Solnhofen slate form thixotropic systems with water and aqueous solutions if the right amounts of both components are mixed. The phenomenon is not only found in the case of water and hydrophilic substances; finely powdered mercaptobenzothiazole, an accelerator, forms thixotropic mixtures with organic liquids such as gasoline, benzene, and alcohol (v. Recklinghausen, *Kolloid Z.*, **60,** 34 (1932)). A thixotropic, viscous, concentrated sol may readily be obtained with a solution of gelatin of suitable concentration; its viscosity is considerably reduced by shaking or pressing through a capillary, and assumes the original value when left at rest (Freundlich and Abramson, *Z. physik. Chem.*, **131,** 278 (1928)).

It is not easy to explain these thixotropic phenomena. They are found in systems where the particles are capable of binding thick layers of liquid around themselves. The amount of liquid must be sufficient to allow the particles to maintain lively Brownian movement, with marked translations when the particles are distributed at random, which means that the system must be fluid after shaking. The particles must, however, also be able to settle and orient themselves in such a fashion that attractive forces prevent any distinct translatory Brownian movement, while a large amount of liquid is enclosed by the gel formed. This reasoning suggests that thixotropic systems are loosely packed. The manner in which particles can pack must be appreciated if thixotropy is to be understood. Although the propositions furnished by mathematics refer to systems of a much simpler kind, it seems worth while to take them into account. The following degrees of packing may be distinguished, when the particles are spherical, not too small, and of equal size (Manegold, Hofman, and Solf, *Kolloid Z.*, **56,** 142 (1931)): the extremes are a very close packing, one sphere always touching 12 neighboring ones, and a very loose packing, one sphere only touching 4 other ones; there are three further intermediate cases, where one sphere touches 10, 8, or 6 neighbors. The relative volume not filled by the spheres but by the medium of dispersion increases rapidly when the packing becomes looser; it changes from 0.26 for the case of closest packing to 0.66 to that of loosest. Though the systems found in nature are much less simple, often containing particles not strictly spherical and of unequal size, it may be assumed as a fairly general rule that the relative volume of the interstices increases when the packing becomes looser. The question of packing is also important in the case of the volume of sedimentation. If the particles are sufficiently large and heavier than the dispersion medium and if the latter is in excess, the particles settle and occupy a certain sedimentation volume. This is, as a rule, a good indication of the closeness of packing; if the volume of sedimentation be small, the packing is close and *vice versa.* In all cases where thixotropic phenomena are found in systems having relatively coarse particles, thixotropy and a large volume of sedimentation are inseparable phenomena, both resulting from loose packing.

Close packing may also give rise to a characteristic phenomenon, described by Reynolds (*Phil. Mag.*, **20,** 469 (1885)) when discussing the behavior of moist sea-sand. When trodden underfoot or pressed, it turns dry and hard, becoming moist again as soon as the pressure is released. According to Reynolds, the original condition of the system is one of close packing, the amount of fluid being just sufficient to fill the interstices. When the particles are displaced by one-sided

pressure, the packing becomes less close, the volume occupied by the interstices increases, and the amount of liquid is not sufficient to fill them entirely; therefore the sand appears dry and is brittle and hard, owing to the increase of friction. On releasing the pressure the particles return to their original close packing, the fluid is able to fill the interstices, and the sand appears moist again. This Osborne Reynolds phenomenon has been observed in the case of other moist powders, such as finely ground quartz and starch (Wo. Ostwald, *Klein. Praktikum d. Kolloidchem.*, 5th ed., p. 80). If the powder is mixed with a suitable amount of water on a glass-plate, and is then compressed with a spatula in forming a heap, it turns hard and dry. Left to itself, water exudes again slowly, a process which may be accelerated by gently tapping the plate and thus inducing the particles more rapidly to assume their original close packing.

Obviously a moist mass showing this Reynolds phenomenon cannot be plastic, and since the system becomes hard and brittle when deformed, it just lacks that property characteristic of plasticity, *i. e.*, that it is soft and easily deformable, but nevertheless retains its consistence. Plasticity in this sense, *i. e.*, isothermal plasticity as it is met with in moist clay, etc., is only found in disperse systems when they are sufficiently loosely packed; such systems may therefore also show a tendency to be thixotropic. It is mainly this isothermal plasticity of disperse system which is the subject of this paper. The following phenomena and properties are likely to appear under similar conditions (Freundlich and Juliusburger, *Trans. Faraday Soc.*, **30**, 333 (1934)):

(*a*) Close packing, small sedimentation volume, Reynolds phenomenon, no plasticity, no thixotropy.
(*b*) Loose packing, large sedimentation volume, no Reynolds phenomenon, plasticity, thixotropy.

So far few systems have been investigated from this point of view, but all agree well with this scheme. Pure quartz powder in water and aqueous solutions belong to the first group, clay and a slate Solnhofen in Bavaria to the second. Foreign substances may strongly influence this behavior. For instance, a non-plastic, non-thixotropic mixture of quartz powder and water may be made plastic and thixotropic by adding a suitable amount of lecithin (Freundlich, *J. Soc. Chem. Ind.*, **53**, 223T (1934)). The latter substance is adsorbed on the surface of the quartz particles; as a hydrophilic colloid it binds water, and the layers formed in this way may cause loose packing and the other phenomena correlated with it.

Some investigators believe that plasticity and thixotropy are inseparable phenomena (McMillen, *J. Rheology*, **3**, 179 (1932); cf. Pryce-Jones, *J. Oil & Colour Chem. Assoc.*, **17**, 313 (1934)). One is perhaps more justified in saying that they both involve loose packing, but that the range of existence for each is somewhat different, though the ranges may overlap; plasticity is favored by higher concentrations of the disperse phase, thixotropy by lower concentrations.

This more formal treatment on the basis of the packing of particles leads to a correlation of thixotropy with other phenomena; but it does not explain why a system containing so much of a liquid phase that it behaves as a fluid (suspended particles having a lively Brownian movement), may also behave, without change in the amount of liquid, like a solid mass or gel, the particles no longer showing marked translations. This is not easily understood. Some assume that the particles remain separated from each other in the gel too, there being very thick layers of liquid between them (in a thixotropic concentrated suspension of bentonite the thickness of these layers may be calculated to be about 0.1 μ). The

particles would be kept in place by an equilibrium of attracting and repelling forces acting between them. Long reaching forces of repulsion are well known; they are due to the electric repulsion between the ionic atmospheres surrounding the particles. But it is not easy to account for the long reaching forces of attraction. It has been generally supposed that the van der Waals forces causing attraction between molecules fall off rapidly and become extremely weak in a distance greater than the diameter of a molecule, *i. e.*, 0.1–1 mμ. But London and Kallmann (*Naturwissenschaften*, **20,** 952 (1932)), applying new conceptions of the quantum theory to the van der Waals forces, consider it probable that these forces of attraction increase with growing particle size and do not decrease so strongly with increasing distance from the surface. According to this theory and for particles of the size found in thixotropic gels and suspensions, a weak, but nevertheless sufficiently large force may still be active in a distance up to 0.1 μ and more. It is difficult to test this theory in thixotropic gels, but it may be possible to do so by determining the adhesion between small solid particles and a wall in a liquid medium.

Other investigators do not assume that the particles in the solid systems are all separated from each other, but prefer the supposition that threads or a network of particles is formed which assures both a solid structure and the enclosure of large amounts of liquid (cf. Kuhn, *Z. physik. Chem.*, A, **161,** 26 (1932)). The ultra-microscopic and microscopic results of different investigators do not agree as to the structure of thixotropic gels. Usher (*Proc. Roy. Soc.*, A, **125,** 143 (1929)) on the one hand describes a definite structure, whereas experiments by others (Szegvari and Schalek (*loc. cit.*); Hauser (*Kolloid Z.*, **48,** 57 (1929))) seem to prove that no distinction can be made between the particles, for though apparently separated by thick layers of liquid they have all lost their Brownian movement in the gel, and resume it again on shaking or stirring. Certainly it cannot be denied that possibly amicronic particles are instrumental in forming a network.

Thixotropy is a fairly general property, but is often limited to a rather narrow region of concentrations of the disperse phase of the electrolyte, etc. The shape and mechanical properties of the particles are presumably of great importance. A non-spherical shape (rods or plates) and a distinct rigidity probably favor the formation of thixotropic systems.

Thixotropy and Plasticity in Systems Containing Rubber

Thixotropic phenomena are frequently met in the colloid chemistry of rubber. Preserved and concentrated latex never seem to turn thixotropic spontaneously; they always retain the properties of a liquid, though it may be a very viscous liquid, but by adding foreign substances, latex is easily transformed into a thixotropic system. A certain amount of lithium sulfate (British patent 342,469 (1931)) or of aluminum sulfate (Pryce-Jones, *loc. cit.*) added to latex preserved with ammonia, is able to do so. Latex is a complicated system, and it is therefore difficult to decide why the aluminum salt, for instance, acts in this way. It might be by a direct lowering of the charge of the particles, as in the case of the metal-hydroxide sols mentioned above, or a more indirect influence of a similar kind caused by the formation of positively charged aluminum hydroxide in alkaline solution; the change in behavior might also be due to an interaction between the aluminum salt and the proteins of the latex.

A thixotropic behavior may also be produced by adding substances naturally prone to form thixotropic suspensions in aqueous solutions. The most efficient substance of this kind is bentonite (British patent 342,469 (1931)), a mineral of

high degree of dispersion, originating from decomposed volcanic ashes which have been transported by the wind as a very fine dust. In structure it is like a zeolite having a rigid skeleton of alumino-silicate anions, besides mobile exchangeable cations of an alkali or an alkaline earth. Bentonite is probably the only inorganic substance known which is able to swell in water and aqueous solutions. A maximum of swelling is found near the neutral point (perhaps a little toward the alkaline side), and at the same point there is an optimum in the thixotropic behavior (Buzagh, *Kolloid Z.*, **47**, 223 (1929); Hauser, *loc. cit.*; Freundlich, Schmidt, and Lindau, *Kollchem. Beihefte*, **36**, 43 (1932)). The common cause of both phenomena is most probably the formation of thick layers of water of hydration round the large particles of this colloidal electrolyte. A characteristic degree of dissociation may be ascribed to it, and this property goes parallel with the degree of hydration, *i. e.*, with the ability to swell and to be thixotropic. The conditions in preserved and concentrated latex as to alkalinity are most suitable for producing thixotropic mixtures with bentonite.

Attempts have been made to use them for technical purposes, as a coagulant dip or for molding (British patent, *loc. cit.*; private communication from Hauser). In the first case the form is dipped into the well stirred thixotropic mixture, and is then removed slowly, the rate being adjusted so that the layer covering the form turns solid as it leaves the mixture. Then the article is dried and vulcanized. If the thixotropic mix is used for molding purposes, it is filled into the mold in a liquid state; after a short time the excess is poured out, a thick layer adhering to the walls of the mold. In this way the hollow article desired is made.

There is no doubt that the examples discussed so far are cases of thixotropy. Other phenomena noticed when treating rubber have been attributed to thixotropy, but they are not equally obvious. One is the well known fact that well masticated, plastic rubber, left to itself regains in course of time some of its original elasticity, as if a structure which had been destroyed by milling had been formed anew. This has been assumed to be a thixotropic change (cf. Hauser, *Liesegang's Kolloidchem. Techn.*, 1st ed., p. 248), and there is a certain resemblance to the case mentioned above, when a concentrated solution of gelatin, which on stirring or pressing through a capillary had become less viscous, regained its original high viscosity when left to itself. Yet mastication is a complicated procedure, where heat and oxidation may be hardly less instrumental in causing the changes observed than the purely mechanical treatment. It is therefore perhaps doubtful whether in this case the most characteristic feature of thixotropy, namely, that it is an isothermal, reversible transformation, is realized.

The cases discussed first, when thixotropic masses were used for molding purposes, are good examples of the near correlation between thixotropy and plasticity; it is the plasticity of a heterogeneous system which is essential in these cases. The influence of lecithin upon rubber mixtures (British patent 389,480; 389,485 (1931)) is possibly also due to phenomena of this kind. It was mentioned above that lecithin is able to make a non-thixotropic, non-plastic mixture of fine quartz powder and water distinctly thixotropic and plastic. It has been known for a long time, for instance, in manufacturing the so-called porcelain of Réaumur, that organic colloids, such as soft soap or glue, may make otherwise non-plastic mixtures of powders and aqueous solutions sufficiently plastic to be molded. Lecithin is markedly adsorbed on surfaces; it has further a strongly polar structure and therefore an affinity to water on the one hand, but also to hydrophobic organic substances on the other. The layer of lecithin on the surface of the quartz will bind a certain amount of water molecules, and thus will produce that loose packing

necessary for the thixotropic and plastic behavior observed. The softening effect of lecithin is recognized in the case of chocolate mixtures (Rewald, *Bull. Office internat. fabr. Choc. Cacao*, **1**, 133 (1931); Rewald and Höfling, *ibid.*, **2**, 69 (1932)); it is claimed for putty (German patent 560,606 (1930)) and for rubber mixtures. It is probable that in all these cases softening is due to the same cause, though it has not been proved, in the case of chocolate and rubber, that the same effect is obtained in a truly isothermal process.

Gutta-percha is a substance where plastic properties are perhaps still more essential technically than is the case with rubber, but the plasticity of gutta-percha is obviously non-isothermal plasticity; it becomes soft and plastic at higher temperatures and turns hard and tough again on cooling. X-ray investigations at different temperatures (Hauser and Susich, *Kautschuk*, **7**, 120, 126, 145 (1931)) have proved that it is amorphous (*i. e.*, similar to a very viscous liquid) at high temperatures, but shows a Debye-Scherrer-diagram, due to the formation of a large number of small crystals distributed at random, below 68°. In this case the substance is easily deformed at higher temperatures, when it is practically a highly viscous liquid, and is made again sufficiently rigid by cooling it rapidly to temperatures at which it is a microcrystalline solid. It would be interesting to investigate whether this type of plasticity is also influenced by substances like lecithin, etc., or whether non-isothermal plasticity may be distinguished from the isothermal plasticity of heterogeneous systems by not being so sensitive toward the addition of foreign substances of this kind.

Thixotropy may prove to explain other phenomena indirectly associated with rubber technology. It has been found important in paints and varnishes. Oil paints containing pigments in suspension are frequently thixotropic, and a certain degree of thixotropy may be valuable (McMillen, *loc. cit.; Ind. Eng. Chem.*, **23**, 676 (1931)); the particles of the pigments do not clog so easily to a hard cake in course of time, and on the other hand a freshly painted layer may solidify quickly enough to guarantee the even distribution of the paint, yet the time necessary for solidification may nevertheless be long enough to ensure that surface tension forces shall be able to smooth out the brush-marks. Now rubber, or especially rubber compounds such as oxidized rubber, is added frequently to paints (Stevens and Heaton, *Trans. Inst. Rubber Ind.*, **9**, 247 (1933)). This new ingredient seems to be advantageous in some cases, because it changes the thixotropic behavior of the paint or is able to call it forth; flat or matt paints are most likely an example of this kind. They contain a high proportion of pigment and little oil, and due to this composition the pigment has a tendency to settle, and the brush-marks cause a striated appearance on the painted surface. On adding a suitable amount of oxidized rubber, or milled rubber plus an oxidizing agent, the paint mixture loses these defects, it retains its consistency for many weeks and may be brushed out freely. Apparently the rubber or rubber compound has an effect similar to lecithin and other colloids favoring plasticity, yet here under undoubtedly isothermal conditions. In absence of the rubber compound the pigment, *i. e.*, the disperse phase, and the oily liquid, *i. e.*, the medium of dispersion, have a strong tendency to separate; on adding the rubber compound they become inseparable. The particles of the pigment are most likely coated by the rubber compound, and are thus enabled to bind a larger amount of liquid, and a thixotropic suspension is formed. Consequently the particles do not settle so quickly, and on the other hand the time of solidification is sufficiently long to allow the brush-marks being smoothed out by surface forces.

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The Oil Resistance of Rubber. I.

Study of the Swelling of Vulcanized Rubber

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1. Introduction

Though ethylene polysulfide resins and Duprene have high resistance to mineral oils, they have some drawbacks, namely, the former has a bad odor and several inferior properties, and the latter is of high price. Some work on obtaining oil-resisting rubber by mixing various oil-resisting substances with natural rubber have hitherto been undertaken by some investigators, such as Ishiguro (*Rubber Chem. and Tech.*, **6**, 278 (1933)), Naunton, Jones, and Smith (*Trans. Inst. Rubber Ind.*, **9**, 169 (1933)), etc., without any success.

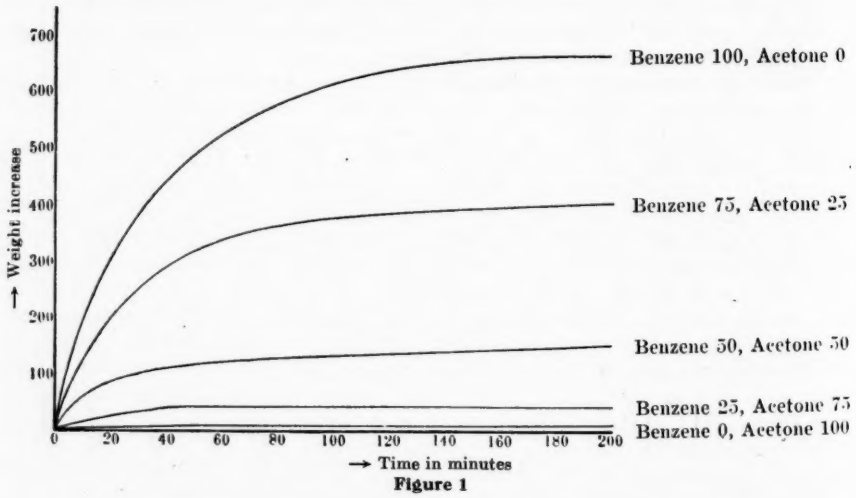

Figure 1

To obtain oil-resisting rubber, it seems to be necessary to study more fully the swelling mechanism of rubber, both raw and vulcanized, especially from the standpoint of the relation between the swelling and the elastic properties of vulcanized rubber. Tiltman and Porritt (*India-Rubber J.*, **78**, 345 (1929)) have published a paper on the effect of solvent in vapor state on the stress-strain curve of vulcanized rubber. The effect of solvent in the liquid state remained unstudied, though probably of more importance for the oil resistance of rubber from the practical point of view. This paper concerns these problems.

2. Experimental

A. Swelling by a Mixed Solvent.—All tests were made with rubber rings of 42 mm. internal diameter, 0.9 mm. thick, and 16.5 mm. wide, prepared by curing

100 parts of smoked sheet and 5 parts of sulfur in a vulcanizing press. The samples were immersed in mixed solvents of benzene and acetone in an air thermostat at 25° C., removing periodically, wiping, and then weighing. The composition of the mixed solvent, time-swelling curves, and swelling maximum obtained by various mixed solvents are shown in Fig. 1.

B. Stress-strain Curve of Swollen Rubber.—It was found that any swelling maximum from zero to 665 per cent can be obtained by using a mixture of ethyl alcohol and benzene as the swelling medium, as shown in Fig. 2. The several swollen rubbers thus obtained were used to determine their stress-strain curves. The results are shown in Fig. 3.

C. Time-swelling and Deswelling Curves.—The relation between the weight increase and elongation of immersed samples in the mixed solvent is very regular, as shown in the following table.

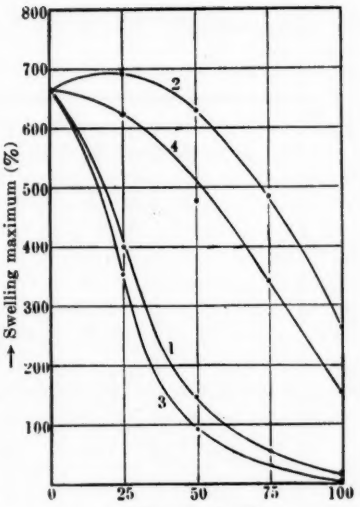

Figure 2

No. of Curve	Diluent
1	Acetone
2	Petroleum ether
3	Ethyl alcohol
4	Ethyl ether

Immersion Time in Minutes	Elongation $\Delta L\%$	Weight Increase $\Delta W\%$	$\Delta W/\Delta L$
0	0	0	
5	26	106	4.1
10	40	182	4.5
20	54	264	4.9
30	64	321	5.0
50	73	364	5.0
80	80	403	5.0
100	82	410	5.0
120	83	415	5.0
150	84	420	5.0
180	85	424	5.0
200	85	424	5.0

From this result, it could be said that the degree of swelling of vulcanized rubber can be expressed by the ratio of the increase in weight to the time of immersion, as well as by the elongation of the immersed sample. Accordingly, the elongations of the samples in a solvent were observed, and after the swelling maxima were obtained, the shrinkages were observed as deswelling took place. The deswelling was brought about by drying the swollen samples in a current of air. The time-swelling and deswelling curves show typical hysteresis loops and residual sets, as shown in Fig. 4. The greater was the weight applied during swelling and deswelling, the greater were the swelling maximum and the residual set. The swelling maximum was increased by repeating the swelling under a constant load, but the deswelling curve showed no change by this repetition, as shown in Fig. 5. This increase in the swelling maximum diminished gradually on repeatedly swelling and

deswelling, and after five times, the time-swelling curve is represented by the same curve.

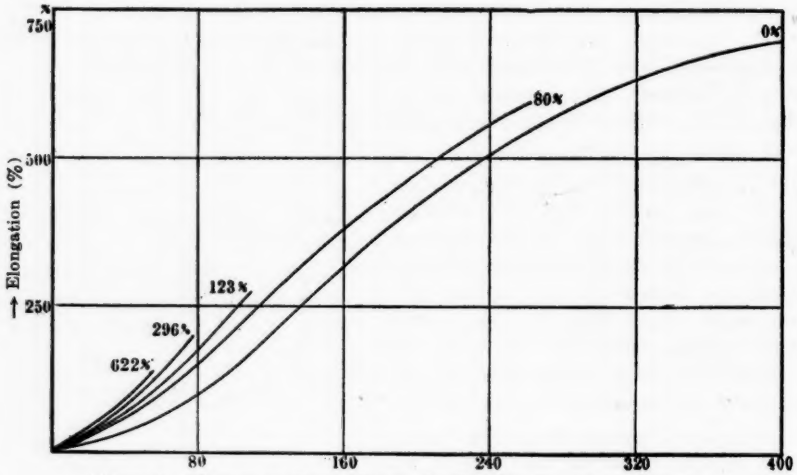

Figure 3. Figures on Curves Mean the Swelling Degree of Samples

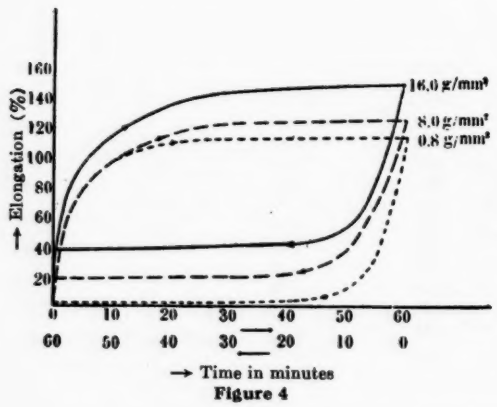

Figure 4

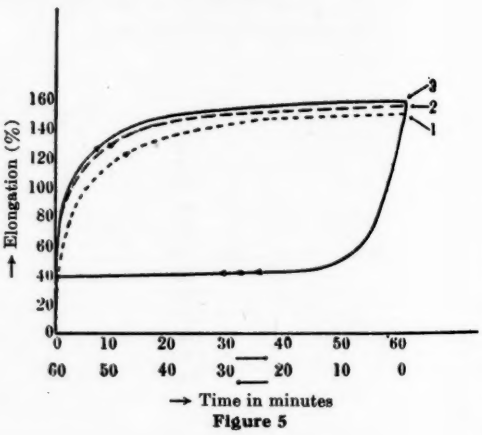

Figure 5

3. Discussion

The S-form of the stress-strain curve of raw rubber found experimentally was explained by Fikentscher and Mark on the basis of the spiral theory (*Kautschuk*, **6**, 2 (1930)) in the following way. In the first part of the curve up to about 80 per cent elongation, a great force is necessary to open the spiral against the van der Waals forces, because the double bonds lie very close to one another. The curve begins, therefore, with a steep ascent. The force increases in proportion to the elongation, while one spiral after another is elongated into the extended chain. The final again-rapidly-ascending branch of the curve corresponds to the large work of elongation of the crystallites already formed. Fikentscher and Mark explained the swelling as follows. The molecules of the swelling agent or solvent

penetrate among the coiled spirals, resulting in a stretching of the primary valence chains during swelling.

These theories may be applied to vulcanized rubber. As shown in Fig. 3, the stress-strain curve of vulcanized rubber before swelling has the S-form. As the degree of swelling increases the first part of the curve straightens, and the final elongation becomes smaller. This change in the first part of the curve is caused by saturation of the residual valences with molecules of solvent, and the decreased elongation results from a release of the coiling, of the spiral molecules. This release is shown by the residual set after deswelling, the magnitude of which is proportional to the tension, as shown in Fig. 4. The swelling maximum becomes greater on repeating swelling and deswelling, whereas the residual set remains constant. These facts indicate that the first swelling releases fully the entanglement of the molecules, and though molecule spirals are opened further by the subsequent swelling, the tendency to coil again is not retained.

Thus, the lowering of the elastic properties of vulcanized rubber may be investigated from two points of view. First there is the molecular affinity for the solvent, and secondly there is the release of the spiralling of the solvated molecule. From these considerations, it seems reasonable that rubber derivatives having high polarities or fewer residual valencies should show less molecular affinity for oil.

4. Summary

To study the effect of solvents on the elastic properties of vulcanized rubber, the following three points were investigated.

1. The swelling maximum obtained by various mixed solvents.
2. The stress-strain curves of rubber swollen to different degrees.
3. Time-swelling and time-deswelling curves.

The spiral theory of molecular structure of rubber proposed by Fikentscher and Mark is utilized to explain the experimental results.

[Reprinted from the Journal of the American Chemical Society, Vol. 57, pages 2318–2321, November, 1935.]

Natural and Synthetic Rubber. XV. Oxygen in Rubber

By Thomas Midgley, Jr., A. L. Henne, A. F. Shepard and Mary W. Renoll

The harmful effects of oxygen on rubber have long been known, and the formation of peroxides during milling has been qualitatively demonstrated.[1] However, quantitative measurements of the oxygen have never been made, and the nature of the oxygen compounds has not been investigated.

Rubber frequently has been analyzed by combustion and the ratio of the carbon percentage to the hydrogen percentage has invariably been found to correspond closely to a $(C_5H_8)_n$ formula. However, it does not follow that such is the formula of rubber. In every instance, the total of the carbon and the hydrogen content has fallen short of 100%. The deficiency is very small, especially in the case of pure rubber, but it invariably exists. The best analyses available, those of the Bureau of Standards,[2] done on highly purified, and on recrystallized rubber, show a deficiency of 0.3%. This cannot be accounted for entirely by contamination of the samples, nor can the combustion be assumed to be that inaccurate. It is logical to regard this deficiency as the oxygen and nitrogen content of the sample.

In the present work, the quantity of oxygen present in rubber samples has been measured by means of the combustion method described by the Bureau of Standards; an effort has been made to determine the type of oxygen present and to study the progressive oxidation of rubber. The technique of the Bureau has been altered in only

(1) Busse, *Ind. Eng. Chem.*, **24**, 140 (1932).

(2) Smith, Saylor and Wing, *Bur. Standards J. Research*, **10**, 479–92 (1933).

TABLE I

ANALYSIS OF RUBBER BY COMBUSTION

Calcd. for $(C_8H_8)_n$, %	H, 11.84	C, 88.16	H/C = 0.13436
Synthetic rubber, found	11.82, 11.83 and 11.83	88.17, 88.17 and 88.17	.1342
Natural rubber, found	11.86 and 11.86	88.07 and 88.07	.1346

Basis of Calculation: C = 12.0048, H = 1.0081 and O = 16.0000.

Note: The samples of natural rubber contained 0.007% N.

TABLE II

NATURAL RUBBER (SOL RUBBER)
(Nitrogen content = 0.007%)

Material	Analyses, % Ash	C	H	H/C	Oxygen content measured by Combustion	Active H	Mol. wt. cryoscopy
Original	0.01	88.07	11.86	0.1346	0.06	0.028	∞
Milled 1.5 hours	.065	87.71	11.79	.1344	.44	.095	∞
Degraded 1 day	.02	87.58	11.75	.1342	.65	.16	∞
Degraded 7 days	.02	82.45	11.05	.1340	6.48	1.51	4400
			SYNTHETIC RUBBER				
Original	0.00	88.17	11.83	0.1342	0.00	0.00	∞
Degraded 1 day	.01	88.14	11.83	.1342	.02	.00	∞
Degraded 11 days	.01	85.43	11.47	.1343	3.09	.91	∞
Degraded 18 days	.03	84.73	11.34	.1338	3.90	1.49	8100
Degraded 31 days	.00	79.40	10.60	.1335	10.00	2.88	4300

two details: (1) a Jena combustion tube was substituted for the Pyrex tube, to prevent sintering at the high temperature used to burn out the last traces of carbon; (2) weighings were improved to ±0.00002 g.

Procedure

Sol rubber was prepared and purified by fractional precipitation[3] until it contained only 0.007 ± 0.0003% of nitrogen by Nessler titration. A sample of this rubber was analyzed by combustion to determine the H/C ratio and the oxygen and nitrogen content by deficiency. Another sample of the same specimen was treated with methylmagnesium iodide and the resulting methane measured to determine the amount of active hydrogen. The amount of carboxylic or ketonic groups present was investigated by treating a third sample with thionylmagnesium iodide, purifying the reaction product and analyzing it for sulfur.[4] The data are listed in Tables I and II together with the results of the same methods used on purified sodium rubber and on the degraded products of both.

Discussion of the Results

The striking fact shown by the tables is that pure synthetic rubber is oxygen free, while natural rubber purified to the same extent by the same procedure contains oxygen; this oxygen is associated with an appreciable amount of active hydrogen while CO groups or oxygen of a peroxide nature are practically absent. Consequently, the experimental results may be interpreted as establishing the presence of an hydroxyl group in what has heretofore been called a hydrocarbon.

In view of the fact that oxygen is measured by deficiency, and its order of magnitude is very small, it is proper to question the significance of the experimental results.

First, may not the deficiency, as determined by

(3) Midgley, Henne and Renoll, THIS JOURNAL, **53**, 2733 (1931).
(4) Midgley, Henne, Shepard and Renoll, *ibid.*, **56**, 1325 (1934).

the combustion, be purely an experimental error in the case of undegraded rubber?

This objection is refuted by the fact that a sample of sodium rubber has been repeatedly analyzed in the same apparatus and manner to give zero deficiency within the probable limits of experimental error.

Second, may not all of the oxygen found in undegraded rubber be attributed to an unremoved impurity?

Such an assumption is refuted by the fact that purified natural rubber gels when it is treated with a Grignard reagent; this is a test for combined oxygen in rubber, as previously shown.[5]

Third, could the combined oxygen be the result of slight degradation during fractionation? This is unlikely because synthetic rubber, which degrades quite easily, was subjected to the same method of purification, yet remained free of oxygen.

Fourth, is the combined oxygen a natural part of the rubber molecule or is it the result of slight oxidation between the time the latex left the tree and the time fractionation started?

The present results are only conclusive for the particular sample used. This sample was taken from the center of a bale of sprayed latex rubber and showed no visible signs of oxidation such as could be seen at the surface of the bale. Similar samples had been investigated previously by fractionation and no evidence of degradation had been found. It is probable, therefore, that the combined oxygen is a part of the rubber molecule occurring in nature.

Irrespective of its origin or significance, combined oxygen has been demonstrated to be present in the natural rubber investigated.

Quantitative Value of the Data

No quantitative significance is attached to any minor variation of the data except for the original undegraded sample of natural rubber and the

(5) Midgley, Henne and Shepard, THIS JOURNAL, 56, 1156 (1934).

oxygen-free synthetic; hence, this part of the discussion is confined to these two.

The values selected for the atomic weights of hydrogen and carbon are important and affect the results. The latest reported values by Aston, namely, 1.0081 for hydrogen and 12.0048 for carbon, have been used in the calculations.

The deficiency of the natural rubber analysis is determined as 0.06%. This value includes the combined oxygen of the rubber and all the oxygen and nitrogen of the impurities present. The samples contained 0.007% of nitrogen. Previous experience with the fractionation of rubber has shown that the nitrogen impurities which are soluble in benzene and alcohol mixtures are easily eliminated but that an insoluble nitrogenous material collects in a gel phase. By degenerating the gel rubber this impurity may be collected. It contains two atoms of oxygen for each atom of nitrogen and behaves as an amino acid. It is almost certain that this impurity is the source of the nitrogen found, hence the total nitrogen and oxygen external from the rubber molecule itself becomes 0.023%. This leaves the combined oxygen as 0.042%.

The results of the treatment with thionyl Grignard were of no significance. The method is no more accurate than the values obtained. And even though these values were other than experimental error, they still would not represent any more oxygen than that available for this reaction in the nitrogen impurity. If there is any ketone, aldehyde or carboxyl oxygen present in the original L. S. rubber, this investigation fails to disclose it.

The hydroxyl oxygen, as disclosed by active hydrogen measurements, is more reliable. This method gives closely checking results. Blanks indicate a high accuracy for acids but a slightly low value for alcohols. If allowance is made for the active hydrogen present in the nitrogen impurity, considered as an amino acid, the final value becomes $(0.028 - 0.008) = 0.02\%$. This value should be looked upon as possibly somewhat

low, as the evidence thus developed points to the rubber molecule being an alcohol.

The value of 0.04% of oxygen as measured by combustion seems somewhat in discrepancy with the value of 0.02% as measured by active hydrogen determination, but a critical study of the possible errors involved in both methods by no means precludes the probability that the true value for the oxygen lies between these two and that hydroxylic oxygen was the only kind of oxygen present in the samples. By computing the molecular weight corresponding to the assumed presence of only one atom of oxygen in each rubber molecule, it is found that 0.04% of oxygen corresponds to a molecular weight of 40,000, while 0.02% corresponds to 80,000 (or 585 and 1170 isoprene units, respectively). This is in substantial harmony with the mol. wt. of 53,000, as determined by sulfur addition,[4] and suggests that the rubber molecule is a high molecular weight member of a pseudo homologous series occurring in nature, starting with geraniol and increasing by isoprene units to rubber.

One definite discrepancy with respect to present-day conceptions of the rubber molecule exists in the data. This is the abnormally high H/C ratio. Experience with the analysis indicates that this ratio is accurate to within ± 0.0001. The theoretical H/C ratio for C_5H_8 with C as 12.0048 and H as 1.0081 is 0.13436. The indicated ratio for the original natural rubber is 0.1346. This is in perfect agreement with the value reported by the Bureau of Standards[2] and is 0.00024 too great, or 0.18% in excess, or one extra hydrogen atom for each 70 isoprene units. This is too small a number of isoprene units for it to be an end-group hydrogen. Likewise, if impurities are assumed to be responsible, a deficiency of 0.18% is required to account for it as water, 0.14% as alcohol or 0.75% of a non-volatile paraffinic hydrocarbon must be present, none of which fits the other data and/or the present accepted theories about the rubber molecule.

Oxidation Data

The data presented relative to the oxidation of rubber are to be taken as merely a preliminary study of the application of the analytical methods used to the problem of the chemistry of the oxidation of rubber. The results are, however, significant. As rubber undergoes oxidation, either by milling or exposure to oxygen and sunlight, the following events occur. The H/C ratio decreases, the combined oxygen increases, the active hydrogen increases and the molecular weight (measured by cryoscopy in benzene) decreases. The thionyl Grignard results still lack significance.

In addition to the data reported, the following experiment was performed. A fresh sample of heavily oxidized rubber was placed in a sealed tube and heated for several hours. Oxygen gas was evolved, the combined oxygen decreased to about half of its original value, the active hydrogen decreased slightly, the H/C ratio decreased and, judging by appearance, the molecular weight had greatly decreased.

These observations and data are sufficient to suggest several deductions as to the probable course of events.

1. Oxygen attaches to the rubber molecule in some peroxide linkage.

2. This linkage rearranges to an OH group with the liberation of O.

3. Some of the OH groups join with H and are eliminated as H_2O; hence the lowering of the H/C ratio.

4. The molecule is ruptured during or as the result of one of the above events.

Experimental

Combustion.—The apparatus developed by the Bureau of Standards[2] was used with the following alterations. A Jena Supremax tube was welded to a large Pyrex slip-joint at one end, and this joint was used without lubricant to connect to the purifying train. All combustions were done in air. Generally a platinum boat was used, but undegraded natural rubber was burned without a boat.

Preparation of the Samples.—Sol rubber samples were obtained by fractional precipitation, handled and stored as previously described.[3] The synthetic rubber samples were prepared from purified isoprene by polymerization over Na–K, *in vacuo*. Polymerization was so rapid that cooling was needed to prevent explosions.

Degradation.—Rubber cement (5% in benzene) was placed in an oxygen-filled round-bottom flask, and exposed to sunlight at room temperature. Dry oxygen was fed periodically to make up for the amount used.

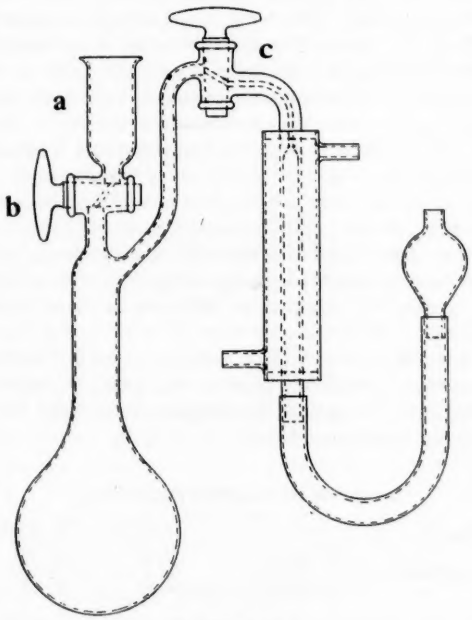

Fig. 1.

Active Hydrogen Determination.—The apparatus was made of sealed Pyrex glass (see Fig. 1), the reaction chamber (a) being an ordinary 300-cc. Kjeldahl flask; the buret (b) was about 7 cc. in capacity and was kept at a known temperature by means of a water circulation jacket.

The reagents used were:

(1) Rubber cement in C. P. benzene. This benzene, which is also used as a wash liquid, must be run as a blank to determine its methane liberation value.

(2) Methylmagnesium iodide in butyl ether, of approximately 1.5 molecular concentration. This reagent is rid of all incidental gases by evacuation and is kept in sealed ampoules containing 7-cc. portions until it is ready to be used. One ampoule is used for each determination.

(3) C. P. triphenylcarbinol, for standardization.

Procedure.—Fill the buret completely with mercury; close the stopcock (c); evacuate the flask completely through (a); place a quantity of rubber cement in (a), such that it will generate from 1.5 to 3.5 cc. of methane; suck it into the flask, and wash (a) with C. P. benzene several times, until the total volume in the flask is about 200 cc. Heat cautiously with a small flame, while evacuating steadily through (a), and shaking vigorously, until the volume is reduced to about 50 cc.; close (b) in such a manner that a small amount of benzene distillate remains above it as a seal. Place the batch of methylmagnesium iodide in (a); reduce it to about one-half of its volume by cautious evacuation, in order to remove any possible gases; allow this reagent to be sucked into the flask, closing (b) just in time to retain a small portion above it as a seal. Heat the mixture cautiously, while shaking frequently; this causes the methane to collect in the side-arm, from where it can be drawn into the buret, together with a small amount of benzene. Close (c), and allow the flask to cool slightly; then reheat with shaking. By watching the ring of benzene condensation rising in the side arm, it is possible to ascertain whether or not more methane is being liberated. Usually two or three successive heatings are sufficient, after which pure benzene reaches the buret. The amount of gas in the buret is then measured, corrected for standard conditions, for benzene vapor and for the previously determined blank.

ANALYSIS OF TRIPHENYLCARBINOL

Sample, g.		0.0322	0.0370
Methane, cc.	Calcd.	2.77	3.19
	Found	2.53	3.14

Summary

It has been shown that natural rubber contains oxygen, while synthetic rubber is oxygen free. This oxygen appears to be of an hydroxylic type, and its quantity corresponds to about one hydroxyl group for each one thousand isoprene units of the rubber molecule.

Rubber has been allowed to oxidize and a mechanism is proposed to interpret the quantitative data recorded.

Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 11, No. 2, pages 224–238, August, 1935.]

Rationalization of the Hardness Testing of Rubber

J. R. Scott

Introduction.—The object of this paper is to draw attention to the present unsatisfactory state of the hardness testing of vulcanized rubber and the need for standardization of this test, and also to present some results of an investigation into the theoretical basis of hardness testing and the practical significance of hardness measurements.

In this paper the word "hardness" will be used in the sense generally accepted in the rubber industry, that is, to denote resistance to indentation.

The most commonly used types of hardness tester measure hardness in terms of the depth of the indentation made by a rigid ball or blunt pin pressed into the rubber by either a dead weight or a spring. The reading given by such an instrument, usually termed the hardness number, must depend on several variable factors, namely (1) the dimensions of the ball or pin; (2) the weight used to press it into the rubber, or the compression characteristics of the spring in the case of spring-loaded instruments; (3) the direction of the scale of the instrument, *i. e.*, whether the reading increases with the depth of indentation, as in the Pusey-Jones Plastometer, or in the reverse direction, as in the Durometer; (4) the units in which the indentation is measured, *i. e.*, whether in 100ths of a millimeter, 1000ths of an inch, or arbitrary units. In addition to these factors relating to the instrument, the reading must also depend on the dimensions of the rubber test-piece, especially its thickness, the nature of the rubber surface, and the period for which the ball or plunger is pressed on to the rubber before the reading is taken.

Quite a number of hardness testing instruments are in more or less common use, such as the Pusey-Jones Plastometer, the Shore Durometer, the Schopper hardness tester, the Cussons Durometer, the Rubbermeter, and the Tinius Olsen hardness tester (embodying the recommendations of the American Society for Testing Materials), and this list could be quite considerably extended.

All the six instruments mentioned differ from one another in regard to at least one of the variable factors mentioned above. Thus, some are spring-loaded and others loaded by dead weights; the weights and spring calibrations vary from one instrument to another; some indent the rubber by means of balls (all of different sizes) and others by a blunt pin; some give the highest readings on the softest rubbers and others the reverse; and some measure the indentation in 100ths of a millimeter and others in 1000ths of an inch. Moreover, where an arbitrary scale has been adopted there has usually been no attempt to make it agree with the readings of some already well-known instrument.

The result is that a hardness number means nothing unless the instrument used is mentioned, and even then it is not of much practical use to anyone not possessing the instrument in question. It is thus clear that hardness testing is in an unsatisfactory state as compared with, say, tensile testing, where the results represent, at least to a reasonable approximation, definite and universally understood properties of the material under test.

Significance of the Hardness Test.—It is necessary at this stage to consider what

information the hardness test may be expected to give about a rubber, and thus what practical value attaches to the measurement of hardness.

It can be shown theoretically (see below) that the resistance to indentation of an elastic isotropic body depends solely on the elastic modulus of the body at small deformations, its dimensions, and the dimensions of the body which indents it. This suggests the possibility of using the hardness test to measure the modulus of rubber at small deformations.

In many uses of rubber, *e. g.*, pneumatic tire treads, solid tires, shoe soling, and all kinds of cushioning and shock-absorbing devices, the elastic behavior at small deformations is of far greater importance than its behavior at some very high elongation, such as is involved in tensile testing, but which is never even remotely approached in use. Moreover, as hardness tests can usually be made on a finished rubber article without damaging it, whereas tensile tests cannot, the hardness test has by far the wider field of application. Clearly, therefore, it would be very useful to be able to employ a hardness test to measure the elastic modulus of rubber at small deformations. Before this can become a practical proposition, however, it will be necessary to adopt a standard form of test and method of expressing the results, and to know how the reading obtained in the standard test is related to the modulus of the rubber.

Standardization.—The first step in the rationalization of hardness testing is, therefore, the standardization of the test. It is interesting at this point to see what has already been done in this direction. Three standard hardness test methods already exist, those of the United States Bureau of Standards (*Bureau of Standards Circular*, No. **38**, p. 91), the American Society for Testing Materials (*A.S.T.M. Tentative Standards* **1932**, p. 995), and the Deutsche Verband für die Materialprüfungen der Technik (*Kautschuk*, Special Number, May, **1926**). These three methods all agree in using a ball pressed into the rubber by a dead weight, but in other respects they all differ, and so do not give the same reading on the same rubber, as is shown below:

	Bureau of Standards	A.S.T.M.	D.V.M.T.
Diameter of ball	1/8 inch*	3/32 inch	10 mm.
Weight	1 kilo	3 lb.	1 kilo
Unit of measurement	0.01 mm.	0.001 inch	0.01 mm.
Reading, relative to Bureau of Standards as 100	100	57	57

* 1/4 inch for very soft rubbers.

The result is that the efforts at standardization up to date have not led to much unification. Moreover, none of the existing standards is British, and it may, therefore, be suggested that the British Standards Institution might render a service to the rubber industry by setting up a standard definition and method of test for the hardness of rubber.

The details of the suggested standard test will not be discussed here, but it will probably be agreed that the best form of instrument for adoption as a standard is one that uses a dead weight, not a spring, and a blunt form of indentor such as a ball, rather than an elongated plunger or pin.

Assuming that a recognized standard test had been adopted, there would still be the problem of interpreting the results in terms of the elastic modulus of the rubber. It is therefore necessary to determine how the result depends on all the variable factors involved, of which the principal are: the modulus of the rubber, the diameter of the ball, the magnitude of the indenting force, and the thickness of the rubber.

An investigation of this subject has been undertaken, and the main results so far obtained are set forth below. The influence of the thickness of the rubber has not yet been examined systematically.

Theory of the Indentation Test.—The force required to make an indentation in a piece of rubber is conveniently regarded as the sum of the "indenting force," required for the purely local deformations involved in forming a hollow in the rubber surface, and the "compressive force," required to compress the rubber between the indenting ball and the rigid supporting surface. On an infinitely thick piece of rubber the compressive force is zero, because any finite compression represents only an infinitesimal strain. The indenting force is therefore the force required to produce a given indentation on an infinitely thick piece of rubber.

As the present experiments deal with relatively large thicknesses of rubber, it is only necessary to consider the indenting force. This force is determined by the dimensions of the indentation and the resistance of the rubber to deformation, *i. e.*, the "hardness modulus," which is conveniently expressed as a ratio of stress to strain. As the indentation is part of a sphere, its dimensions may be expressed in terms of a size factor, *i. e.*, the radius of the sphere, and a shape factor, *i. e.*, the ratio of the depth of the indentation (H) to the radius of the sphere (R). The indenting force (D) is thus a function of the hardness modulus of the rubber (M), the radius of the ball (R), and the shape factor (H/R); expressed mathematically:

$$D = \psi(M, R, H/R) \tag{1}$$

In this and later equations ψ denote some unknown function of the quantities in brackets.

Hardness Modulus.—This, being a ratio of stress to strain, must have the dimensions of force/length;[2] D obviously has the dimensions of a force. In equation (1) D and M are the only quantities involving force, hence D must be proportional to M, other things being equal. Equation (1) can therefore be written:

$$D = M.\psi(R, H/R) \tag{2}$$

Indentation can lead only to three types of deformation, *viz.*, extension, compression, and shear (assuming plastic deformation to be absent). The hardness modulus must, therefore, be a combination of the extension modulus (E), compression modulus (C), and shear modulus (S); that is:

$$M = xE + yC + zS \tag{3}$$

where x, y, and z are numbers depending on the relative extents to which the three types of deformation are involved, that is, they depend solely on the shape of the indentation, and are thus functions of H/R. Friction between the ball and the rubber must have some influence on the distribution of strains, and hence on x, y, and z, but tests have shown this influence to be small on relatively thick rubber samples.

For small strains, such as are involved in the indentation, the extension and compression moduli are substantially equal (Morrison, *Trans. Inst. Rubber Ind.*, **7**, 112 (1931); Sheppard and Clapson, *India Rubber J.*, **82**, 312 (1931); Hencky, *Rubber Chem. and Tech.*, **6**, 217 (1933); this can also be demonstrated theoretically). In an isotropic incompressible elastic material the shear modulus equals one-third of the extension modulus (Southwell, "Dictionary of Applied Physics," Glazebrook, Vol. I, p. 245). Equation (3) therefore becomes:

$$M = xE + yE + zE/3$$

and since x, y, and z are functions of H/R:

$$M = E.\psi(H/R)$$

Combining this with equation (2) gives:

$$D = E.\psi(R, H/R) \qquad (4)$$

This equation shows that the force required to produce an indentation of given dimensions is proportional to the modulus of the rubber at small extensions. Experimental confirmation of this is described below.

Size Factor (R).—The forces required to produce equal strains in objects of the same material and of geometrically similar shape but different sizes are proportional to the squares of corresponding linear dimensions of the objects. Hence, for a given shape of indentation (H/R constant) the force must be proportional to the square of the size factor. Equation (4) therefore becomes:

$$D = ER^2.\psi(H/R) \qquad (5)$$

Shape Factor (H/R).—The relation between indenting force and shape factor, other things being equal, has not yet been deduced theoretically. It has been shown experimentally (see below) that when the compressive force is relatively small, the total force (F) required to produce the indentation is proportional to $R^2(H/R)^{1.35}$. For a given ball size, therefore, F is proportional to $(H/R)^{1.35}$ and hence the indenting force (*i. e.*, F − compressive force) must also be very nearly proportional to this quantity. The expression ψ (H/R) in equation (5) is thus approximately equal to $(H/R)^{1.35}$.

Experimental

Rubbers and Methods Used.—Many of the rubbers will be referred to by serial numbers; relevant particulars of these are given in Table I.

Except where otherwise stated, tests were made with the R. A. B. R. M. hardness gage (Daynes, Johnson, and Scott, *Trans. Inst. Rubber Ind.*, **6,** 63 (1930)); the period of application of the load was 30 seconds, except for the earlier tests (paragraph 2) where 60 seconds was adopted. Every figure recorded is the mean of 5 or 6 readings, or more where great accuracy was required or the consistency was not very good.

As the experiments were intended as an investigation of the indenting force only, conditions were chosen so as to minimize the compressive force. The indentation was therefore kept small compared with the thickness of the rubber.

Relationship between Modulus of Rubber and Indenting Force.—This relationship has not previously been investigated directly, but some authors have examined the relationship between modulus, usually measured at a fairly high elongation, and the depth of indentation under a given load (Zimmermann and Brown, *Ind. Eng. Chem.*, **20,** 216 (1928); Gurney and Cameron, *India Rubber J.*, **71,** 554, 601 (1926); Ariano, *L'Industria,* **43,** Nos. 17–19 (1929)). The results of these different workers, however, are so widely divergent that no general conclusion can be drawn from them.

Experiments were made to test the theoretical deduction that the force required to make an indentation of given dimensions on an infinitely large mass of rubber is proportional to its modulus at small extensions. An "infinite" mass of rubber cannot, of course, be obtained, but as the compressive force is proportional to the

extension modulus, other things being equal, the total force required to produce the indentation on a finite piece of rubber must theoretically be proportional to this modulus. In practice, therefore, finite pieces of rubber are satisfactory for the present purpose.

TABLE I

No.	Type of Rubber	Shape	Thickness Mm.	Hardness (*a*)
1	.....	disc 4.5 cm. diam.	9	21
2	.....		9	44
3	.....		9	50
4	.....		9	85
5	.....		9	110
6	.....		9	135
7	Gray buffer	disc 8 cm. diam.	25	44
8	Gray buffer	disc 8 cm. diam.	25	48
9	Tire tread (gas black)	slab 10 × 8 cm.	13	56
10	Tire tread (soft black)	slab 10 × 8 cm.	13	104
11	Carbon black mix	disc 4.5 cm. diam.	5	44
12	Brown sole	disc 4.5 cm. diam.	5	20
13	Tire tread	disc 4.5 cm. diam.	5	60
14	Black sole	disc 4.5 cm. diam.	3.5	10
15	Flooring	large sheet	10	33
16	Flooring	large sheet	3	25
17	Zinc oxide mix	disc 4.5 cm. diam.	5	56
18	Magnesium carbonate mix	disc 6 cm. diam.	12	100
19	Solid tire	section of tire, c. 12 × 10 cm.	30	65
20	Rubber-sulfur	disc 6 cm. diam.	10	160

Note: (*a*) depth of indentation (mm/100) by 1/4-inch diam. ball under 1 kg. load

Forty-two rubbers covering the whole usual range of hardness were selected, and tests made on discs 45 mm. diam. and 9 mm. thick to determine the load (L) required to produce an indentation 0.50 mm. deep with a ball 1/4 inch in diameter. The modulus (E) was determined by finding the load required to stretch a ring test-piece to an elongation of 5 per cent. With heavily compounded rubbers some difficulty was experienced, owing to the rubber exhibiting plastic flow under load.

The values of E and L are plotted against one another in the accompanying figure (logarithmic scales are used for convenience in showing the wide range of values). The broken line represents the theoretical correlation curve (L proportional to E), and it will be seen that the points lie approximately along this line. Deviations from exact proportionality can be attributed, in part at least, to the following causes: (1) existence of grain in the rubber, especially the harder ones at the upper end of the graph; the modulus was measured in the plane of the sheet from which the rings were cut, whereas the hardness test involves the modulus perpendicular to this plane; (2) existence of plastic flow in the very stiff rubbers, which makes it difficult to measure the modulus exactly and is not taken into account in the theoretical consideration of the subject.

It may be concluded that, within the limits of accuracy imposed by the nature of the rubbers, the force required for a ball of given size to make an indentation of given depth is proportional to the modulus of the rubber at small extensions, in accordance with the theoretical equation (5).

Relationship between Depth of Indentation and Indenting Force. (Test Series A).— Rubbers were tested each with several loads, usually ranging from 100 to 1000 or 1500 grams, the specimens and loads being chosen so that the indentation never exceeded one-fifteenth of the thickness of the rubber.

As the indentations under the smaller loads were necessarily very small, it was thought that errors might arise from the method used to obtain the zero setting, *i. e.*, pressing the boss of the gage on to a glass plate and depressing the ball till it just touches the plate (see Daynes, Johnson, and Scott, *loc. cit.*). If a rubber sample is not perfectly flat the boss rests on the higher portions, and the ball may thus have to be depressed slightly below the zero position before it touches the rubber. The reading, therefore, tends to be high, the error being proportionately greater the smaller the load.

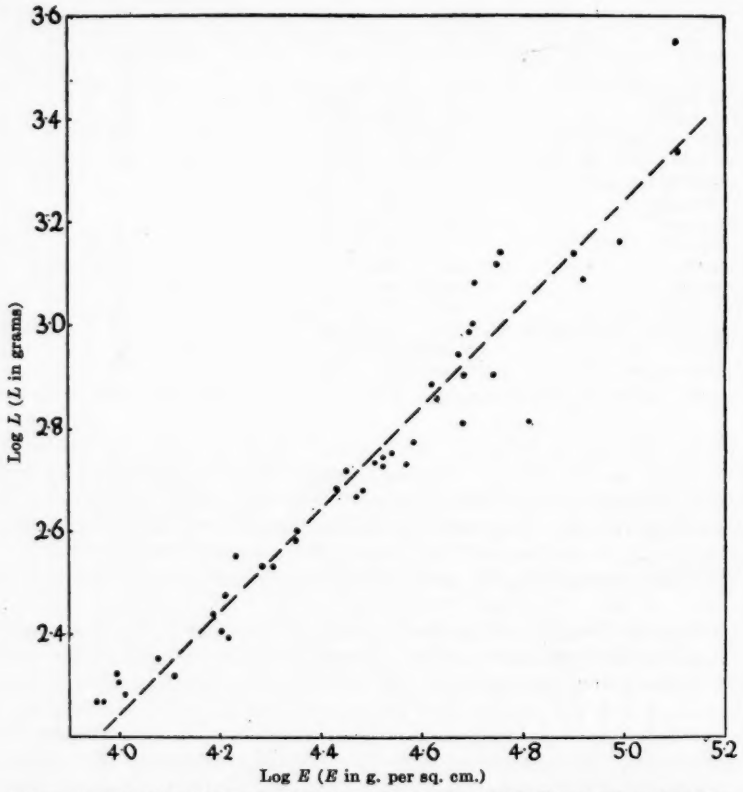

Figure 1. Relation between Modulus (*E*) and Load (*L*) Required to Produce a Given Indentation

Some tests were accordingly made with another method of zero setting that eliminates this error. The gage stem is pressed down lightly till the ball just touches the rubber, and this position is taken as the zero. This can be done fairly accurately, so that the zero setting can be repeated to within 0.01 mm. Some force must, however, be acting on the ball when it is felt to touch the rubber, so that the zero reading corresponds to a slight indentation, and the final hardness reading tends to be low.

When the logarithm of the hardness reading is plotted against the logarithm of the load, a straight line is obtained, showing that the indentation (H) is related to the load (F) by an equation of the type $H = F^n \times$ constant.

Table II gives the results obtained with the two methods of zero setting: (*a*) on the glass plate, (*b*) on the rubber. The following points will be noted: (1) Method (*b*) gives higher values of n than method (*a*), as would be expected because the zero setting errors tend to make these methods give too high and too low values, respectively; the true value of n must, therefore, lie between 0.74 and 0.77. (2) The $^1/_8$-inch ball gives slightly higher values than the $^1/_4$-inch, though the difference is scarcely significant in view of the experimental error. (3) The value of n does not vary with the hardness of the rubber.

TABLE II

Rubber	Ball Diameter Inch	n (Method *a*)	n (Method *b*)
1	$^1/_4$	0.77	..
2	$^1/_4$	0.70	..
3	$^1/_4$	0.73	..
4	$^1/_4$	0.79	..
5	$^1/_4$	0.76	..
6	$^1/_4$	0.72	..
7	$^1/_8$	0.74	0.79
7	$^1/_4$	0.72	0.76
8	$^1/_8$	0.72	0.76
9	$^1/_8$	0.78	..
9	$^1/_4$	0.76	..
10	$^1/_8$	0.72	..
10	$^1/_4$	0.70	..
11	$^1/_8$	0.73	..
12	$^1/_8$	0.74	..
Mean		0.74	0.77

(*Test Series B*). In a few of the log F/log H curves in Series A there was a slight deviation from linearity at small loads. Further tests were, therefore, made to ascertain whether the relationship deduced from Series A is exactly true when the indentation (and hence H/R) is very small.

Tests were made on very hard rubbers 5 mm. thick, using loads such that the indentation never exceeded 0.2 mm. Results obtained by methods (*a*) and (*b*), described under Series A, are given in Table III.

TABLE III

Rubber	Ball Diameter Inch	Method	Identation (Mm./100) Under Load (Grams) of: 20	50	100	200	n
11	$^1/_8$	*a*	...	...	12.8	20.3	0.67
11	$^1/_8$	*b*	...	...	10.4	18.0	0.79
11	$^1/_8$	*a**	...	...	13.7	22.1	0.70
11	$^1/_8$	*b**	...	...	12.3	20.4	0.74
11	$^1/_4$	*a*	...	...	8.9	14.8	0.73
11	$^1/_4$	*b*	...	...	7.3	13.0	0.83
12	$^1/_8$	*a*	...	...	10.6	17.2	0.69
12	$^1/_8$	*b*	...	...	8.0	13.2	0.72
12	$^1/_4$	*a*	...	...	7.1	11.6	0.71
12	$^1/_4$	*b*	...	...	6.0	9.7	0.70
13	$^1/_8$	*a*	4.5	8.8	16.1	..	0.78
13	$^1/_4$	*a*	3.2	6.5	11.4	..	0.78
		Mean for method *a*		...	..		0.725
		Mean for method *b*		...	..		0.755

* Repeat tests made some time later.

Although the individual values of n vary considerably, as is natural with such small indentations, the means for methods (a) and (b) are close to those in Series A. This shows that even at very small indentations there is no radical departure from the force-indentation relationship applicable to larger indentations.

(*Test Series C*). To eliminate any difficulty of obtaining an accurate zero setting, experiments were made by a differential method, *i. e.*, measuring the difference between the indentations produced by a small load f and a much larger load $F + f$. This difference obviously cannot be influenced by errors in the zero setting.

It has been shown above that under conditions such that the compressive force is negligible, $H = kF^n$. If h is the difference between the indentations produced by the loads f and $(F + f)$, it is easily shown that:

$$\log h = k_1 + \log [(F_0 + 1)^n - 1]$$

where $F_0 = F/f$ and k_1 are a constants. For values of n of the order of 0.75 the curve of log h plotted against log F_0 is practically straight (actually slightly convex to to the log h axis) when F_0 is above about 5; the slope of the curve depends on the value of n.

From tests with various values of F, keeping f constant, experimental log F_0/log h curves can be drawn. These, like the theoretical ones, are straight or slightly convex to the log h axis. By plotting theoretical curves for various values of n and comparing these with an experimental curve, the value of n for the latter can thus be determined. Results so obtained are shown in Table IV.

TABLE IV

(f = 23 Grams)

Rubber	Ball Diameter Inch	n	Range of Loads (F) Grams
7	1/8	0.76	100–1500
7	1/4	0.755	100–1500
8	1/8	0.73	100–1500
9	1/8	0.775	200–1200
9	1/4	0.745	200–1200
10	1/8	0.725	100–1000
10	1/4	0.715	100–1000
11	1/8	0.735	100– 500
12	1/8	0.73	200–1500
	Mean	0.74	

As in Series A, n does not vary with the hardness of the rubber, and the 1/8-inch ball again tends to give slightly higher n values than the 1/4-inch.

Conclusion.—The data for the value of n are summarized as follows:

Average by zero-on-glass method (Tables II and III)	0.735
Average by zero-on-rubber method (Tables II and III)	0.76
Average by differential method (Table IV)	0.74

Values have been calculated also from data published by Zimmermann and Brown (*loc. cit.*), Ariano (*loc. cit.*), and Daynes, Johnson, and Scott (*loc. cit.*); these range from 0.65 to 0.85, the average being 0.74. As the zero-on-glass and zero-on-rubber methods are known to give low and high values respectively, 0.74 may be accepted as the most probable value. Thus, on a given rubber with either 1/8 or 1/4-ball—

$$H = F^{0.74} \times \text{constant}$$

TABLE V

Load = 1000 grams except where otherwise stated.
RA = R.A.B.R.M. hardness gage; Pl = Pusey-Jones plastometer;
PM = Strachan's piezomicrometer.

Indentation (Mm./100)			
1/8-Inch Ball	1/4-Inch Ball	Ratio r	Instrument Used
4.5	3.2	1.4	RA (20 grams)
8.8	6.5	1.35	RA (50 grams)
9.3	6.6	1.4	RA (100 grams)
9	6	1.5	RA
11.6	8.1	1.43	RA (100 grams)
12	8.5	1.4	Pl
13	8.5	1.53	RA
15.2	10.7	1.42	RA (200 grams)
16.1	11.4	1.41	RA (100 grams)
19.2	13.9	1.38	RA (200 grams)
20	13	1.55	RA
20	15.7	1.27	Pl
21	17	1.25	Pl
23.5	16	1.47	RA
23.7	16	1.48	Pl
23.5	17	1.38	PM
24.5	18	1.36	RA
26.0	18.8	1.39	Pl
26	19	1.37	Pl
28	18	1.55	PM
29	18.5	1.55	RA
27.8	21.4	1.30	Pl
29	20.5	1.41	Pl
29	21	1.38	Pl
30.5	21.4	1.42	Pl
30.7	21.2	1.45	Pl
40	27	1.48	RA
50	37	1.35	Pl
54	38	1.42	Pl

Relationship between Ball Diameter and Indentation. (*Test Series D*).—Table V gives the values of the ratio (r) between the 1/8-inch and 1/4-inch ball readings obtained prior to the present investigation. Values from Table III (mean for methods *a* and *b*) are included also.

Although individual values of r vary considerably, owing to the relatively large errors in measuring small indentations and the fact that many of the tests were not made primarily with a view to obtaining accurate values of r, there is no tendency for r to vary with the hardness of the rubber.

The mean of the values of r in Table V is 1.415. As the errors must be larger for the smaller indentations, it might be considered more accurate to take the ratio of the sum of the 1/8-inch readings to the sum of the 1/4-inch readings; this gives $r = 1.41$, very close to the first-named value.

(*Test Series E*). As the data for the R.A.B.R.M. gage in Table V were obtained with the zero setting on glass, which may introduce errors as already explained, further tests were made by the differential method, described above, to eliminate these errors. It can readily be shown that the value of r for differential readings must be the same as that for readings taken in the normal way.

Results are given in Table VI for numerous tests, in which the depth of indentation never exceeded one-fifteenth of the thickness of the rubber.

TABLE VI

(f = 23 Grams)

Rubber	Indentation (Mm./100) 1/8-Inch Ball	1/4-Inch Ball	Ratio r	F Grams
7	9.1	6.6	1.38	100
11	9.9	7.4	1.34	100
11 (*b*)	10.4	7.3	1.42	100
14	14.3	10.3	1.40	1000
15	14.2	10.5	1.35	200
7	16.3	11.7	1.39	200
11	18.0	13.0	1.38	200
16	20.0	14.8	1.35	500
9	21.0	15.6	1.35	200
9 (*a*)	20.1	14.9	1.35	200
17	24.0	17.1	1.40	200
17 (*b*)	23.0	16.5	1.40	200
18	23	18	1.38	100
10	24.5	18	1.36	100
19	28.8	20.5	1.40	200
7	29.5	21.1	1.40	400
9	29.8	22.0	1.36	300
7	34.7	25.6	1.36	500
10	41.5	31.0	1.34	200
7	45.4	33.8	1.35	700
9	46.7	32.9	1.42	500
7 (*c*)	58	42.5	1.37	1000
7	59.5	44	1.35	1000
9	60	43.5	1.38	700
20	67.2	48.1	1.40	200
9 (*c*)	72	51.5	1.40	1000
9	80	56	1.43	1000
7	81.5	58.5	1.39	1500
10	85	63	1.35	500
9	93	66	1.41	1200
7	101.5	71.5	1.42	2000
8	107	78	1.37	2000

Notes: (*a*) different sample of the same rubber.
(*b*) repeat test with another gage.
(*c*) tests with Plastometer (f = 85 grams).

It will be noted from the results in Table VI that the value of r does not vary with the depth of the indentation or with the load. The mean of the values of r is 1.380, or if the ratio of the sum of the 1/8-inch readings to the sum of the 1/4-inch readings is taken, r = 1.382.

Conclusion.—The data for the value of r are summarized below:

Average from previous R.A.B.R.M. work (Table V)	1.41
Average by differential method (Table VI)	1.38

Values for this ratio have been obtained by the following authors, or can be calculated from their results: Ariano (*loc. cit.*), Gurney and Cameron (*loc. cit.*), Gurney (*Ind. Eng. Chem.*, **13**, 707 (1921)), Houwink (quoted by van Rossem, *Kautschuk*, **7**, 232 (1931)), Gottschalk (*Kautschuk*, **8**, 144 (1932)), and Daynes and Scott (unpublished experiments). These range from 1.36 to 1.62, the average being 1.41.

Due consideration of these various values according to their probable accuracy gives the best value for r as 1.395.

General Relationship between Force, Ball Diameter, Modulus of Rubber, and Indentation.—The ratio (r) between the indentations made by balls with diameters

in the ratio 1:2 has been shown to be independent of the depth of the indentation. It follows that r is also independent of the absolute size of the balls, provided the ratio of diameters remains the same. The relationship between indentation (H) and radius of ball (R) can therefore be written $H = R^m \times$ constant. The value 1.395 for r gives $m = -0.48$. Hence:

(i) for contant force and ball size: $F = k_1E$ (paragraph 2).
(ii) for constant modulus and ball size: $H = k_2F^{0.74}$ (paragraph 3).
(iii) for constant modulus and load: $H = k_3R^{-0.48}$.

Combining these equations gives: $H = k_4(F/E)^{0.74}R^{-0.48}$, or

$$\frac{F}{E} = KR^{0.65}H^{1.35} \tag{6}$$

(k_1, k_2, k_3, k_4, and K are constants).

From the experimental data plotted in the figure above, the value of K is found to be 2.1 when F is in dynes, E in dynes per sq. cm. and R and H in cm. If F is in kg., E in kg. per sq. mm. and H in mm./100, $KR^{0.65} = 0.0090$ and 0.0057 for $^1/_4$-inch and $^1/_8$-inch diameter balls, respectively. These constants are calculated from the force F required to make an indentation 0.5 mm. deep on 9 mm. thickness of rubber; as a small compressive force is thus involved, the indenting force D must be slightly less than F.

The data plotted in the figure show that the observed values of K and $KR^{0.65}$ may deviate by ± 20 per cent from the values given above. It is not yet known how far these deviations are due to experimental error, or to grain or plasticity in the rubbers, or to other causes.

Interconversion of Readings of Different Instruments.—The results of this investigation make it possible to interconvert the readings of any hardness testers that use spherical indentors under constant loads, whether applied in addition to a small "zero" load, as in the Pusey-Jones Plastometer, or not, as in the R.A.B.R.M. gage. The readings (H_1 and H_2, in the same units) of two instruments using loads F_1 and F_2 applied in addition to "zero" loads f_1 and f_2, and having ball radii R_1 and R_2, are related as follows:

$$\frac{H_1}{H_2} = \frac{[(F_1 + f_1)^{0.74} - f_1^{0.74}]R_2^{0.48}}{[(F_2 + f_2)^{0.74} - f_2^{0.74}]R_1^{0.48}}$$

Where no "zero" load is used the f disappears.

Summary and Conclusions.—1. The hardness testing of rubber is at present in an unsatisfactory state owing to the multiplicity of instruments giving different readings on the same rubber. Attention is drawn to the need for standardization of the test.

2. The force that must be applied to a ball to indent the surface of a large mass of rubber depends on the elastic modulus of the rubber (at small deformations), the radius of the ball, and the ratio of the depth of indentation to this radius. The relation of the force to the modulus and the ball radius, the third factor being constant, is deduced theoretically.

3. Experiments to determine the following relationships are described: (1) modulus and force required to produce a given indentation, (2) force and depth of indentation, (3) ball radius and depth of indentation. These experiments confirm the theoretically deduced relationships between force and modulus (approximately) and between force and ball radius, and show how the force is related to depth of indentation.

4. By means of the relationship between indentation, modulus, force, and ball radius, the elastic modulus of rubber for small elongations or compressions can be calculated from the results of hardness tests. Although the method at present appears to be only approximate, it is sufficiently accurate for many practical purposes, and therefore forms a useful means of determining the modulus in cases where ordinary tensile or compression tests cannot be made.

5. The results obtained make it possible to interconvert the readings of any hardness test instruments that use spherical indentors under definite loads, whether applied in addition to a small "zero" load (as in the Pusey-Jones Plastometer) or not (as in the R.A.B.R.M. gage).

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Porosity in Vulcanized Rubber

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The presence of bubbles or pores in vulcanized rubber constitutes a widely experienced factory problem. This research was undertaken to develop quantitative methods of measuring porosity in rubber vulcanizates, to study individual factors responsible for porosity, and to develop methods of overcoming it under works conditions.

Porosity may occur from a variety of causes, particularly where insufficient pressure is applied during vulcanization. The defects associated with porous rubbers are: unsatisfactory appearance, failure or variability under physical test, electrical breakdown of a length of cable, inferior moisture resistance, inferior aging properties, and inconsistency in service tests. These defects may lead to the scrapping of large production batches, or the abandonment of a mix which gives excellent results in all other respects.

There is, however, little record of the factors causing porosity and methods designed to prevent it. Some indirect information can be obtained from publications on sponge rubbers. Thus a paper from E. I. du Pont de Nemours and Company (*Rubber Age* (N. Y.), **25,** 665 (1929)) refers to the advantages of using pale crepe, which loses its nerve more rapidly than does smoked sheet rubber, and recommends the use of softening fillers and delayed-action accelerators, which assist sponging. Among those making passing reference to porosity, Duncan (*Trans. Inst. Rubber Ind.*, **7,** 380 (1932)) regards curing in French chalk as the most troublesome form of vulcanization (as porosity may occur through uneven heat penetration), and the extrusion of soft mixes which dissolve more air than in normal sheeting as a cause of pores arising during curing. Boussand (*Rev. gén. Caoutchouc*, **88,** 4 (1933)) considers that porosity is the result of the action of heat on the gases liberated during vulcanization and on volatile substances in the mix. This action occurs before the rubber is sufficiently vulcanized to resist gas liberation. Lime, magnesia, and litharge are claimed to reduce porosity. Hill (*Gummi-Ztg.*, **47,** 488 (1933)) states that hot milling generally removes moisture from rubber stocks, but if moisture is present, serious porosity may be produced.

In view of the limited number of these references to the cause of such an important defect, the following investigation was undertaken.

General Procedure.—The rubber for each series of mixes was taken from one consignment of pale crepe; the master batches were masticated on a laboratory mill with 12 inch rolls with a friction speed ratio of 2 to 1, the front roll making 20 revolutions per minute. The batches, masticated to the required plasticity, were subdivided for the mixes dealt with in each section of the work. Each mix was sheeted to a thickness of about 60 mils, either directly from the mill or after calendering. Small samples cut from the sheets were vulcanized by the methods described, and the products examined for porosity visually, by tensile testing, by aging followed by weighing or acetone extraction, by permeability tests, and by specific gravity measurements.

Methods of Vulcanization

Porosity was observed to develop as soon as the rubber "set up" if thick samples were exposed in an oven above 100° C. Under the standard methods of vulcanization the liability of a mix to develop porosity varied widely. Therefore samples were cured under the usual conditions and also under conditions designed to increase porosity.

Molding in a Press.—Products cured in a press were usually free from porosity, if there was sufficient rubber in the mold. Each mix was normally press-cured to provide non-porous samples as a basis for comparison. Also, using a mold of predetermined capacity, samples slightly under- and overweight were vulcanized, to investigate the effect of slight mechanical pressure.

Vulcanization in Open Steam in French Chalk.—Extruded products are usually cured in this way, and frequent waste of material may occur, with subsequent abandonment of an accepted mix. Porosity in these products may be due to properties inherent in the mix, gases entrapped during processing, moisture in the French chalk or condensed from the steam, uneven heat penetration, or use of a long slow rise for bulky products.

Sample mixes were vulcanized in French chalk, first with practically no rise, secondly with a slow rise, and thirdly in damp chalk. The steam pressure was regulated by hand throughout the cures, and mixes found to have widely differing tendencies to porosity were compared. The results given in later sections showed that there was less tendency for porosity to develop in steam than in dry heat cures where no pressure was applied to the rubber. This was probably due to the pressure applied by the steam in the pan. The use of damp chalk or a long, slow rise from cold produced severe porosity in mixes liable to this defect.

Vulcanization of Wrapped Articles in Open Steam.—The prevention of porosity is a serious problem in the manufacture of wrapped products. The factors found to influence this were lack of pressure on the samples during wrapping, the thickness of the rubber sheet, the number of layers of rubber on the mandrel and the closeness of overlapping layers, excessive moisture in the cloth, condensed moisture from the steam, use of a long rise.

Use of Specially Designed Mold.—Experiments on molded samples referred to above, showed that porosity was only likely to develop if the mechanical pressure was below a certain limit. The mold shown in Fig. 1 was designed to ensure the production of a sheet of standard dimensions under easily reproducible conditions, and with practically no pressure applied to the rubber. Its essential features are spew gaps (*a*) evenly distributed around the center flange (*b*), which determines the thickness of the sheet.

The full pressure of a hydraulic press could be applied to the plates so that a sheet of standard thickness (50 mils) was produced; as soon as the rubber became hot and plastic, rapid spewing occurred along all the channels and there was ample space (*c*) provided to receive surplus rubber. The only pressure developed was due to the resistance of the rubber to plastic flow, which, in the early stages of hot vulcanization, was low. Such a mold favored the production of porosity in mixes liable to this defect, and provided a convenient sample for comparison by the various methods of assessing porosity described below. The sheet vulcanized in the mold had to be over 50 mils in thickness to ensure that the mold space was filled, but considerable variation was permissible without affecting the results with soft mixes. All the mixes under examination were vulcanized in this mold, using *a*, calendered sheet, *b*, sheet run straight from the mill with the rolls at friction speed and *c*, after moisture treatment of the uncured sheet.

Dry Heat Vulcanization.—Frequently in manufacturing operations, it is desirable to vulcanize rubber articles by conveying through, or suspending in, a heated chamber where no pressure is applied to the rubber. Porosity is particularly liable to develop under these conditions. This was investigated by vulcanizing

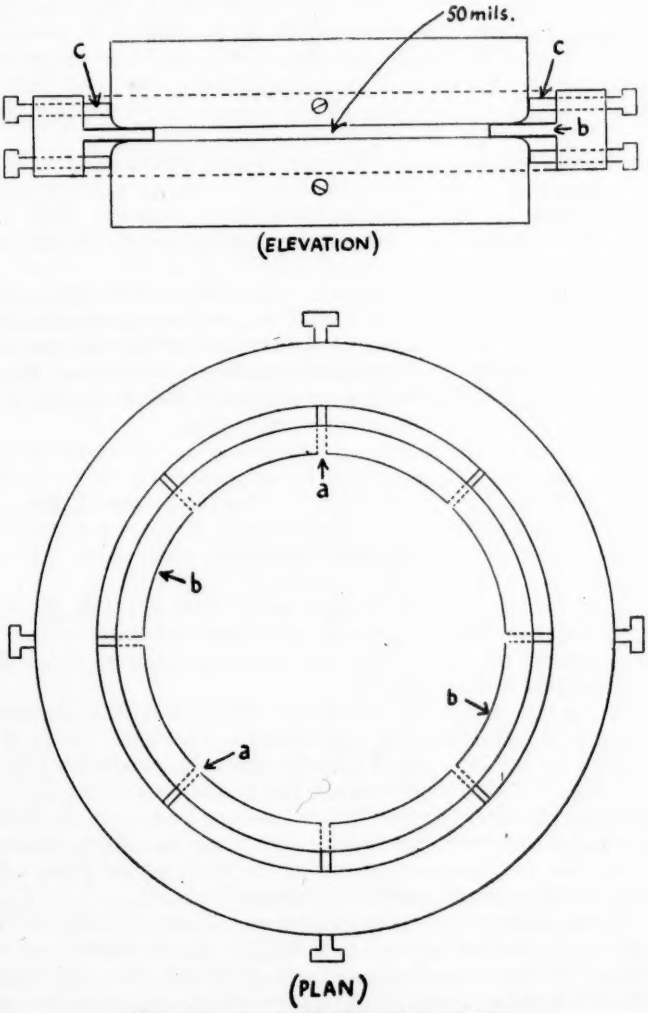

Figure 1. Special Mold for Vulcanization

sheets of various types of mix on a steel plate placed between the slightly open platens of a daylight press, which thus constituted an oven. By direct observation of samples cured in this way, porosity could be seen to develop during the initial stages of vulcanization. A range of samples similar to those treated in the special

mold were cured by this method. Generally, the most severe porosity was produced in rubber vulcanized between open platens in this special mold.

Testing for Porosity

Visual Examination of the Vulcanizates.—The first method of comparing the tendencies of samples to become porous under the above vulcanizing conditions was that of visual examination of the sheet by observation of porosity on the surface, examination of the interior by cutting discs and observing the cut edges, sharp bending to open up surface pores, stretching of the sheet and, when no fillers had been added to render the rubber opaque, by viewing by transmitted light.

Specific Gravity Determinations.—Though visual examination gave a rapid qualitative comparison in the more pronounced cases, an accurate quantitative method was required to detect smaller variations in porosity. The most satisfactory method was found to be the measurement of specific gravity before and after vulcanization.

When the vulcanizates were non-porous, a slight but definite increase in specific gravity occurred during vulcanization. This was greatest in mixes with the highest rubber content and was independent of the hardness of the mix, rate of cure, or mechanical pressure applied. These results confirm conclusions of Kreps (*India Rubber J.*, **84,** 293 (1932)) that there is an increase in specific gravity due to condensation of the rubber molecules during vulcanization.

The inner discs cut by Schopper ring cutters were used as standard test-pieces; specific gravity measurements were made by weighing in air and in water at room temperatures. The results were calculated to the third decimal place and slight porosity in sheets was readily detected, although invisible. A volume change of 0.01 per cent on the disc test-pieces was measurable, whereas for visible porosity, a volume change of 1 to 2 per cent was required.

Samples molded in the press were non-porous and gave a specific gravity increase of about 1 per cent over the unvulcanized mix; these were taken as the basis, and the degree of porosity was expressed as the percentage decrease in specific gravity as compared with the molded samples.

Tensile Testing.—It is generally assumed in tensile tests that fracture is most likely to occur at a point where any imperfection is present. Hence, if a ring is slightly porous, it would be expected to break under abnormally low loads. Numbers of rings were cut from porous sheets, but tensile tests were found unreliable in comparing the porosity. Extremely low breaking loads were obtained in some cases with samples that were only slightly porous and visual examination showed that the break did not necessarily occur at the most porous place. Also some rubbers with obvious porosity gave good breaking loads.

Aging of Porous Rubber.—It was considered probable that the degree of porosity would influence the surface exposed to oxidation and therefore accelerate aging of the rubber. The following simple methods of following the aging were tried.

(*a*) Gain in Weight of Porous Discs during Aging.—Standard disc samples of the base mixes, vulcanized in the special mold, were aged in a Geer oven at 82° C. for periods of 7 and 14 days. The samples were weighed after drying for 2 hours at 82° C. and also after aging. The percentage gain in weight was taken as indicating the degree of oxidation. The results are given in Table I for mixes made with normally masticated and over-masticated rubber, details of which are given in Table IV; the latter was known (from results given in later sections) to yield excessively porous rubbers.

TABLE I

PERCENTAGE GAIN IN WEIGHT OF POROUS SHEETS DURING AGING

Treatment	Cure			Normally Masticated Rubber (A1)		Over-masticated Rubber (C1)	
	Min. Rise	Min. Cure	Steam Press. Lbs. per Sq. In.	7 Days	14 Days	7 Days	14 Days
Molded in press	..	30	40	0.19	1.1	0.33	1.5
In special mold. Calendered:							
Dry sheet	..	30	40	0.61	1.4	0.59	1.4
Normal sheet	..	30	40	0.40	1.5	0.69	1.7
Wet sheet	..	30	40	0.81	1.9	0.82	1.0
	..	90	20	1.3	3.2	0.83	1.8
Normal sheet	30	20	40	1.0	2.3	0.50	1.0
	..	15	60	0.34	1.0	0.83	2.6
Sheet run from Mill:							
Normal	..	30	40	0.46	2.8	0.48	3.0

It was found that the general trend of the weight increases was similar for all the samples and could not be correlated with their porosity.

(*b*) Acetone Extraction of Aged Samples.—By a severe aging test of 14 days at 82° C., the rubber could be oxidized to a considerable extent. In the case of porous samples with increased surface accessible to the air, it was anticipated that the acetone extract would increase more rapidly than with similarly treated non-porous samples. That this was the case is shown by the results given in Table II.

TABLE II

INCREASE IN ACETONE EXTRACT OF POROUS SHEETS DURING AGING

Treatment	Cure		Normally Masticated Rubber (A1)		Over-masticated Rubber (C1)	
	Min.	Steam Press. Lbs. per Sq. In.	Percentage on Mix	Increase	Percentage on Mix	Increase
Before aging	30	40	4.4	...	5.4	...
After 14 days at 82° C.:						
Press cured	30	40	6.7	2.3	8.4	3.0
In special mold. Calendered:						
Dry sheet	30	40	6.6	2.2	9.0	3.6
Normal sheet	30	40	7.2	2.8	12.1	6.7
Wet sheet	30	40	7.3	2.9	10.7	5.3
Normal sheet	15	60	5.5	1.1	11.5	6.1
Sheet run from Mill:						
Normal sheet	30	40	6.8	2.4	14.1	8.7

The acetone extract was chosen as a simple test applicable to a large range of samples, but it is known from the work of Davey (*Trans. Inst. Rubber Ind.*, **4,** 493 (1929); **5,** 386 (1930)) that increase in acetone extract is not an infallible criterion of the oxidation of the rubber, as the resins tend to become insoluble in acetone. The amount of acetone-soluble oxidation product formed on aging is also influenced by the presence of ingredients other than rubber.

Permeability to Moisture.—Increased moisture permeability is one of the characteristics of porous rubbers. An attempt was made to use this property as a measure of porosity in sheet rubbers. A sheet of standard dimensions was clamped over a vessel containing phosphorous pentoxide and the outer surface exposed to a

TABLE III

PERMEABILITY TO MOISTURE OF POROUS SHEETS

Mix	Porosity as Per Cent Increase in Specific Gravity over That of Non-Porous Sample	Moisture Passed after 168 Hours' Exposure to 75 Per Cent Relative Humidity
Normally masticated rubber A1	7.9	2.6 mg. per sq. cm.
Over-masticated rubber C1	12.3	4.8 mg. per sq. cm.

controlled atmosphere of 75 per cent relative humidity. The gain in total weight of the vessel gave a measure of the moisture which passed through the rubber. The results are given in Table III. It was noted that this property was dependent on the porosity of the sheet; but the method is limited in application owing to the difficulty in obtaining exactly comparable sheets.

Factors Influencing the Production of Porosity

Masticating Treatment.—As it was recognized that the degree of mastication was an important factor influencing the occurrence of porosity, special methods of mastication were employed. A series of 1000 gram batches (A1 to A4) was prepared, using the base mix and subjecting pale crepe rubber to the treatments given in Table IV. The rubber used in sample C1 was milled on cold rolls for 60 minutes.

TABLE IV

Batch No.	Treatment of Rubber	Ingredients
A1	15 min. on hot rolls at 50 to 55° C.	Mix:—rubber, 93; zinc oxide, 3; sulfur, 3.2; dibenzothiazyl disulfide, 0.75
A2	90 min. on hot rolls at 85° C.	
A3	5 min. in Banbury internal mixer	
A4	30 min. in Banbury internal mixer	
C1	60 min. on cold rolls	

The degree of mastication was followed by plasticity measurements on small molded discs of masticated rubber in a plastometer as recommended by the Research Association of British Rubber Manufacturers. The rubber sample 0.75 inch in diameter, was placed on a platform 0.5 in. in diameter fixed to the base of the instrument. The plastometer was contained in an oven maintained at 100° C., with a double glass window in the door so that readings could be taken without opening the oven. A 2 kg. weight was applied and allowed to bring the thickness of the sample to 200 mils; the side screw was adjusted to maintain this position for 10 min. so that equilibrium was attained. The side screw supporting the weight was then released and the thickness of the sample read from the dial in mils after 3 and 5 minutes. The plasticities obtained on the above batches are given in the following table and figure; the results on a sample of Ungar-Schidrowitz softened rubber used for mix no. F7 are also included.

TABLE V

Sample	Initial Thickness 200 Mils. Thickness after Time in Plastometer 3 Min.	5 Min.
A1	165	152
A2	129	117
A3	190	176
A4	175	150
C1	49	38
F7 (Softened Rubber)	90	72

It was evident that the rubber softened much more rapidly on cold than on hot rolls. Therefore the over-masticated rubber master-batches C, E, and G, used in subsequent sections were prepared by treating rubber on warm rolls until it ran smoothly, and immediately cooling and masticating on cold rolls for between 60 and 100 minutes to the plasticity obtained with batch C1. Over-mastication on hot rolls or in the Banbury mixer had little influence in increasing the plasticity beyond a certain point, which was readily exceeded by cold mastication.

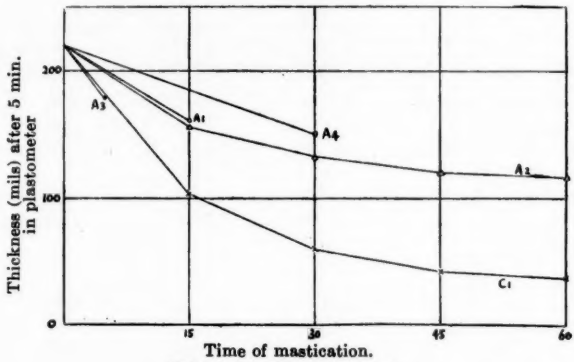

Figure 2. Plasticity Tests

A1. Normal mastication. A2. Over-mastication on hot rolls.
A3. Normal mastication in Banbury. A4. Over-mastication in Banbury.
C1. Over-mastication on cold rolls.

TABLE VIA

DETAILS OF MIXES

Ingredients	B1	B2	B3	B4	B5	C4	C5	D1
Rubber normally masticated	93	93	87	83	73	...	...	50
Rubber over-masticated	...	...	...	...	...	88	88	...
Zinc Oxide	3	3	3	3	3	3	3	3
Sulfur	3.2	2.5	7.5	3	3	3.2	3.2	1.75
Mercaptobenzothiazole disulfide	0.75	1.0	...	0.75	0.75	0.75	0.75	0.4
Tetraethylthiurum disulfide	...	0.5	...	...	...	...	...	...
Magnesia	...	...	2.5	...	...	...	...	...
Paraffin Wax	...	...	...	10	20	...	...	...
Carbon Black	...	...	...	...	...	5	...	...
Light magnesium carbonate	...	...	...	...	...	...	5	...

C1—C3 as B1—B3 but using over-masticated rubber.
D2 as D1 but 58 zinc oxide added.
D3 as D1 but 30 French chalk added.
D4 as D1 but 20 carbon black added.
D5 as D1 but 24 light magnesium carbonate added.
D6 as D1 but 40 titanium dioxide added.
E1—E6 as D1—D6 but using over-masticated rubber.
F1 as B1 but using heat treated rubber.
F2 as B1 but using ozonized rubber.
F3 as B1 but using acetone-extracted rubber.
F4 as B1.
F5 as B1 but 3 of rubber replaced by 3 of Agerite Powder.
F6 as F5 but using heat-treated rubber.
F7 as B1 but using softened rubber.
G1—G6 as F1—F6 but using over-masticated rubber.

Tensile measurements on vulcanizates from severely treated rubbers of the compositions given in Table VIa are shown in Table VIb, and show that the tensile product was only slightly lessened by over-mastication in the Banbury mixer or on hot rolls, whereas it was more seriously reduced in the case of batch C1, in which the rubber was over-masticated on cold rolls.

TABLE VIb

TENSILE PROPERTIES OF MOLDED SAMPLES

Mix	Modulus at 300 Per Cent Elongation Kg. per Sq. Mm.	Tensile Strength Kg. per Sq. Mm.	Elongation at Break Per Cent	Tensile Product
A2. Hot over-masticated	0.11	1.37	840	1150
A3. Banbury mixed	0.13	1.51	810	1225
A4. Banbury over-masticated	0.16	1.54	745	1150
Normally masticated:				
B1. Base mix (also A1)	0.11	1.48	870	1290
B3. Magnesia-sulfur	0.18	1.48	785	1160
B4 containing 10% wax				
B5 containing 20% wax				
Over-masticated on cold rolls:				
C1. Base mix	0.10	1.13	850	960
C3. Magnesia-sulfur	0.09	1.02	910	930
C4. 5% carbon black	0.13	1.65	845	1400
C5. 5% magnesia carbonate	0.21	1.50	715	1060
Fillers in killed rubber:				
E1. Base mix	0.10	1.21	855	1040
E2. Zinc oxide	0.38	1.47	560	820
E3. French chalk	0.35	1.23	620	760
E5. Magnesia carbonate	0.55	1.22	510	620
E6. Titanium dioxide	0.35	1.44	640	925
Pre-treatment of killed rubber:				
G1. Heat-treated	0.10	0.50	605	310
G2. Ozonized	0.13	1.09	720	790
G3. Acetone-extracted	0.10	0.62	685	430
G4. Base mix	0.10	1.11	812	900
G5. Agerite Powder	0.11	1.05	787	830
G6. Heat-treated with Agerite	0.12	1.44	765	1090

In addition, from Table II it may be noted that the aging quality of press cured samples was inferior to that of corresponding samples made with normally masticated rubber. All these results indicated that cold milling is more severe in bringing about disaggregation of the rubber.

Throughout the investigation, the porosity of samples in which the rubber had received a normal mastication was compared with that of those in which it had been over-masticated. Whatever the method of vulcanization or of assessment of porosity, severe over-mastication tended to increase porosity. Figure 3 indicates the relative porosity of batches A1–4 and C1, as judged by decrease in specific gravity.

It was concluded that prolonged mastication on the Banbury mixer or on hot rolls had no marked influence in increasing porosity, but, samples which received prolonged mastication on cold rolls developed the most pronounced porosity in each of the methods of vulcanization. These results were in line with plasticity, tensile and aging results, and confirmed that the most severe disaggregation of the rubber, leads to the most marked porosity.

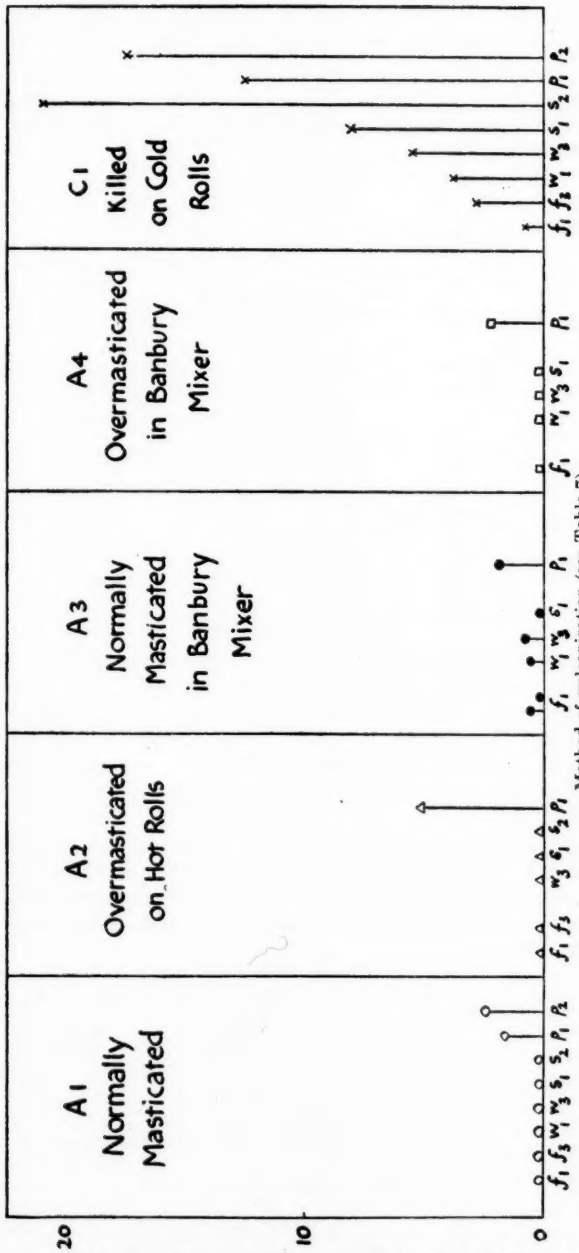

Figure 3. Effect of Mastication on Porosity

Effect of Softeners.—In view of the connection which was found between the porosity and plasticity of a batch, it was of interest to investigate the influence of excessive addition of softener, using normally masticated rubber. Mixes B4 and B5 (see Table VIa) were prepared containing 10 and 20 per cent paraffin wax, respectively, as this softener was unlikely to be affected by vulcanization. In Table VII and Fig. 4 the porosity developed by these mixes is compared with that of the base mixes B1 and C1.

TABLE VII

Vulcanizing Treatment	B1 As A1 Normally Masticated		B4 Containing 10% Wax		B5 Containing 20% Wax		C1 As A1 but Killed Rubber	
	S. G.	% Decrease	S. G.	% Decrease	S. G.	% Decrease	S. G.	% Decrease
Molded in press	0.977	..	0.975	..	0.970	..	0.973	..
In French chalk:								
Run off mill (f_1)	0.970	0.7	0.970	0.5	0.964	0.6	0.967	0.6
Wetted (f_2)	0.968	0.9	0.966	0.9	0.823	14.8	0.947	2.7
Wrapped:								
Run off mill (w_1)	0.978	Nil	0.968	0.7	0.974	Nil	0.938	3.7
Wetted (w_2)	0.966	1.1	0.967	0.8	0.926	3.8	0.921	5.5
In special mold:								
Run off mill (s_1)	0.964	1.3	0.939	3.7	0.874	10.0	0.896	8.1
Run off calender (s_2)	0.943	3.5	...	..	...	..	0.768	21.4
Wetted (s_3)	0.952	2.5	...	..	...	..	0.939	24.4
Between open platens:								
Run off mill (p_1)	0.900	7.9	0.937	3.9	0.960	1.0	0.855	12.3
Run off calender (p_2)	0.852	12.9	...	..	...	..	...	...
Wetted (p_3)	0.894	8.6	0.762	21.8	...	..	0.803	17.7

These results show that the porosity developed by a mix softened with wax is as serious as that in a mix where the rubber is killed on cold rolls. The addition of wax would lessen, rather than increase any tendency for the rubber to combine with oxygen during mastication; therefore the increased porosity was attributed mainly to gases mechanically entrapped in the rubber. It seemed unlikely from this result that the combined oxygen in over-masticated rubber plays any important part in producing porosity.

Effect of Stiffening Agents.—To confirm the results obtained with softeners, mixes C4, C5, E4, E5 were prepared in which stiffening fillers, *e. g.*, gas black free from large quantities of adsorbed gases, and light magnesium carbonate, were added to base mixes made with rubber killed on cold rolls. The results are given in Table VIII and Fig. 4.

TABLE VIII

Mix / Vulcanizing Treatment	C4		C5		E4		E5	
	S. G.	% Decrease	S. G.	% Decrease	S. G.	% Decrease	S. G.	% Decrease
Molded in press	0.997	...	1.004	...	1.145	...	1.185	...
In French chalk:								
f_1 (see Table 7)	...	...	0.976	2.8	...	...	...	...
f_2	1.005	Nil	0.976	2.8	1.141	0.4	1.169	1.5
Wrapped:								
w_2	1.000	Nil	0.962	4.2	...	...	...	...
In special mold:								
s_1	...	...	0.999	0.5	1.136	0.8	1.170	1.4
s_2	0.979	1.8	...	...	1.132	1.2	1.180	0.5
Between open platens:								
p	0.964	3.3	0.950	5.4	...	...	...	...
p_3	0.903	9.5	0.945	5.9	...	...	...	...

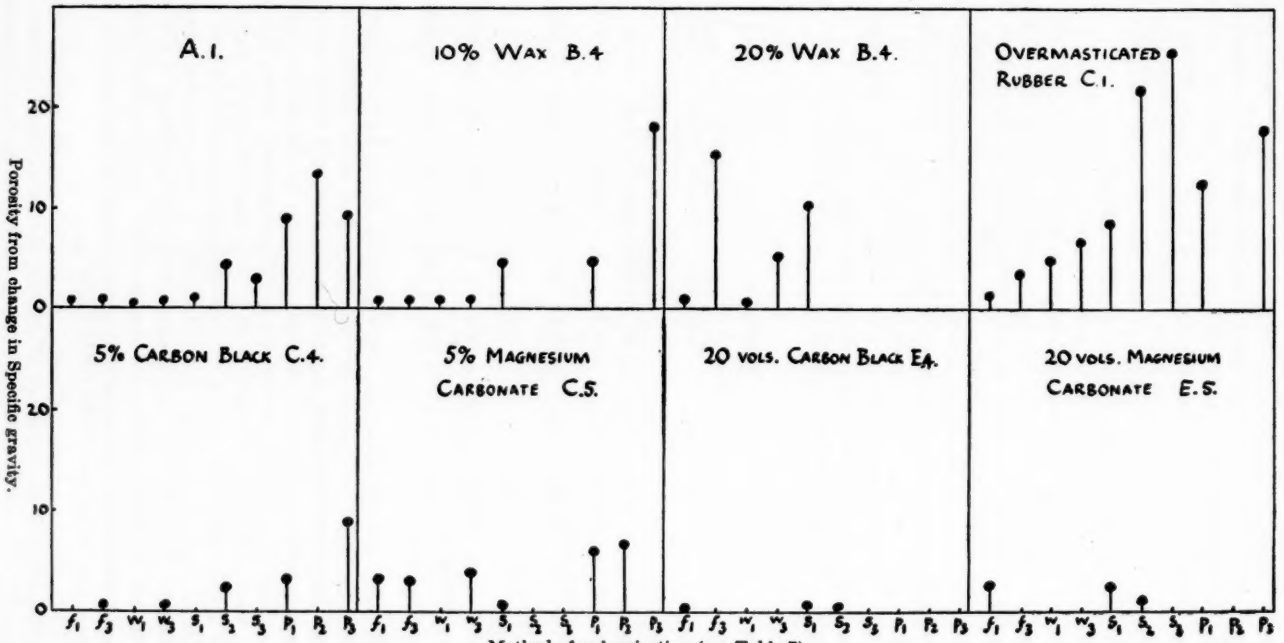

Figure 4. Effect of Softeners and Stiffening Agents on Porosity

The excessive porosity of the base mix C1 was greatly reduced by the addition of 5 per cent by weight of gas black or magnesium carbonate. With 20 volumes loading of these fillers, provided that they were dry and free from much adsorbed gas, no porosity developed even under extreme conditions, such as vulcanization between open platens or in the specially designed mold. These fillers were considered to have a mechanical action in lessening the amount of gas entrapped during milling, through their stiffening action on the rubber. They also increase the resistance to flow during the initial stages of vulcanization.

Effect of Accelerators.—Delayed-action accelerators have been stated to promote sponging, presumably because they allow pores to develop before the rubber stiffens owing to vulcanization. On the other hand, it may be argued that if the rate of aerating a rubber is rapid, as observed during the present experiments with highly porous mixes, a rapid "setting up" of the rubber will retain the maximum porosity and not allow the gas to escape so readily as in the case of a delayed-action accelerator. To investigate these alternatives, mixes B1, B2, B3, C1, C2, and C3 were prepared, using normally masticated and killed rubber with: dibenzothiazyl disulfide as a delayed-action accelerator (B1 and C1); a mixture of this and tetraethylthiuram disulfide as an ultra-accelerator (B2 and C2); and magnesia combined with a high sulfur content to give a slow-curing mix (B3 and C3). The results are given in Table IX.

TABLE IX

Vulcanizing Treatment	B2 As A1 but with Ultra-accelerator		B3 As A1 but with Slow Accelerator		C2 As C1 but with Ultra-accelerator		C3 As C1 but with Slow Accelerator	
	S. G.	% Decrease	S. G.	% Decrease	S. G.	% Decrease	S. G.	% Decrease
Molded in press	0.964	...	1.019	...	0.971	...	0.981	...
In French chalk: f_1	0.964	Nil	1.013	0.6	0.921	5.2	0.979	0.2
Wrapped: w_1	0.965	Nil	...	...	...	...	...	...
In special mold: s_1	0.955	1.0	1.005	1.4	0.888	8.6	0.958	2.3
Between open platens: p_1	0.895	7.2	1.066	Nil	0.800	17.8	0.995	Nil

A comparison of these results with those given in Table VII for mixes B1 and C1, shows that the most severe porosity was developed when an ultra-accelerator was used both in mixes containing normally masticated and killed rubber, cured under the appropriate conditions. A delayed-action accelerator showed which samples were likely to develop serious porosity, particularly when this was due to moisture, which probably escaped more slowly than entrapped gases. High-sulfur mixes accelerated only with magnesia showed little tendency to porosity. This behavior of fast-curing mixes was attributed to the more complete entrapment of gases evolved during the early stages of the heat treatment. The chemical decomposition which occurs in sponge mixes is slower than the liberation of gases dissolved in the mix and a delayed action is required to permit sponging reactions to proceed to a maximum before the rubber sets up.

Effect of Temperature of Vulcanization.—As the activity of the accelerator was shown to influence porosity, the effect of varying the temperature of vulcanization was investigated. The results obtained with a number of the base mixes are given in Figs. 5 and 6, curves being given for mixes A1 (normally masticated rubber),

A2 (rubber over-masticated on hot rolls), C1 (rubber over-masticated on cold rolls), B2 and C2 (ultra-accelerated mixes) and F7 (made with softened rubber). Except where otherwise stated, all these samples consisted of calendered sheet.

When given free opportunity to develop, by curing between open platens with no applied pressure, the porosity increased with rising temperature, thus confirming

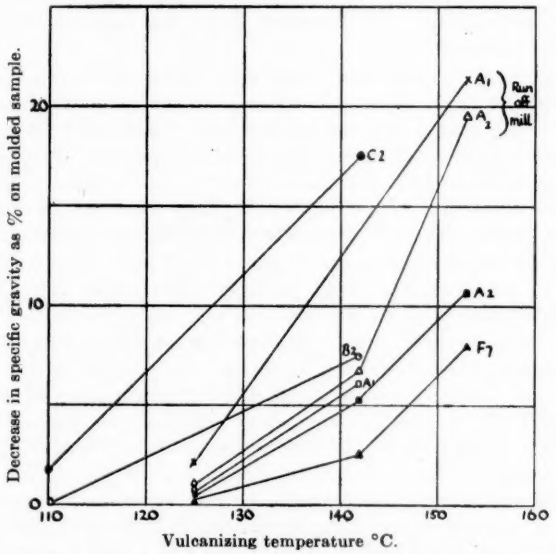

Figure 5. Effect of Temperature on Porosity of Samples Vulcanized between Open Platens

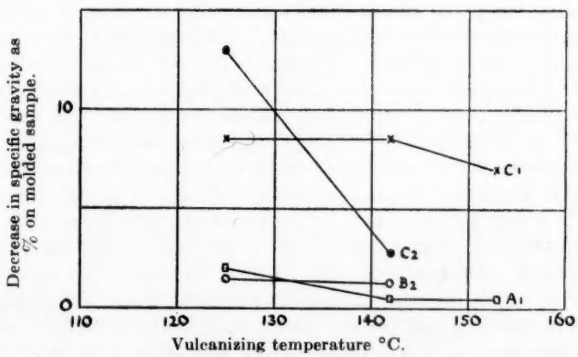

Figure 6—Effect of Temperature on Porosity of Samples Vulcanized in Special Mold

the results obtained with ultra-accelerated mixes. In addition, when slight mechanical pressure was applied, *e. g.*, by vulcanizing in the specially designed mold, the free escape of the gases evolved was hindered, and porosity became equally severe when vulcanizing at 125° or 150° C.

The ultra-accelerated mixes B2 and C2 showed a pronounced decrease in porosity with rising temperature in the specially designed mold. This was probably due to the rapid setting up of the mix, which prevented free spewing and allowed development of sufficient pressure to prevent liberation of gases. Thus the cure approached more closely that of a sample molded under high mechanical pressure. Mixes B2 and C2 gave practically no porosity when vulcanized between open platens at 110° C.; at this temperature, vulcanization was slow, as with an unaccelerated mix at 150° C. Any liberated gases then have ample time to escape before the rubber sets up.

Effect of Fillers.—So far, all the batches had been derived from a base mix containing about 90 per cent rubber. Technical mixes are usually loaded with inert fillers or reinforcing agents to give the required consistency or strength. Two series of mixes were prepared therefore, using 20 volume loadings of each of the main fillers with a normally masticated master batch for mixes D1 to D6 and an over-masticated rubber for mixes E1 to E6. The results of vulcanizing tests on these mixes are given in Table X, from which the following points may be noted.

Fillers in general decreased the tendency for porosity, thus confirming results obtained with stiffening agents. High loadings of zinc oxide (Mix D2) were likely to give almost as porous mixes as the base mix D1 using normally masticated rubber. With French chalk, some porosity was apparent, but gas black, light magnesium carbonate and titanium dioxide gave no porosity under the conditions of test. When the rubber was over-masticated, both titanium and zinc oxides gave very porous products, comparable with those obtained from the unloaded mix E1. This may be attributed to the softening action of these fillers on uncured rubber stocks (Bodger and Cotton, *Trans. Inst. Rubber Ind.*, **8**, 16 (1932)). This action was emphasized by the use of a mercapto accelerator and over-mastication of the rubber. It was also apparent that French chalk only partially overcame the porosity of over-masticated rubber, whereas gas black and magnesium carbonate were far more effective in this respect.

Effect of Chemical Treatment of the Raw Rubber.—The most important result so far obtained was the primary influence of over-mastication in increasing porosity. It has been shown in recent papers that the breakdown of rubber during mastication is mainly due to the action of oxygen. To investigate whether this oxygen taken up during over-mastication was responsible for increased porosity, a series of experiments was carried out with mixes made from raw rubber, which had been heated or chemically treated before mastication, to increase the combined oxygen in the rubber. In mixes F1 to F7, thinly creped raw rubber was subjected to the following seven treatments, respectively, prior to a normal mastication and addition of vulcanizing ingredients: F1, heating at 110° C. for 16 hours; F2, exposure to a slow stream of ozone for 8 hours; F3, acetone extraction for 16 hours; F4, no pretreatment; F5, no pretreatment but 3 per cent. Agerite Powder present during mastication; F6, heating at 110° C. for 16 hours with 3 per cent Agerite Powder present; and F7, the Ungar-Schidrowitz rubber-softening process. A further series of mixes G1 to G6 was also prepared in which the rubber received the above pretreatments, followed by over-mastication. As was expected from the severity of the treatment, mixes G1, G2, G3, and G6 were extremely soft and difficult to handle on the mill, even when cold. Tensile results on press-cured, non-porous samples of these mixes, included in Table VIb, showed that the pretreatment and extreme mastication affected the properties of the rubber after vulcanization. The results of porosity measurements on these mixes after various vulcanizing processes are given in Tables XI and XII.

TABLE X—EFFECT OF FILLERS

Normally Masticated	D1 Base Mix		D2 Zinc Oxide		D3 French Chalk		D4 Gas Black		D5 Mag. Carbonate		D6 Titanium Oxide	
Vulcanizing Treatment	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.
Molded in press	0.981	..	1.728	..	1.273	..	1.128	..	1.175	..	1.431	..
In French chalk:												
f_1	...	..	...	..	...	..	...	..	...	..	1.429	0.2
f_2	...	..	...	..	...	..	...	..	...	..	1.433	Nil
In special mold:												
s_1	0.952	2.9	1.700	1.7	1.240	2.6	1.134	Nil	1.178	Nil	1.427	0.3
s_2	0.960	2.1	1.685	2.5	1.245	2.2	1.126	0.2	1.167	0.7	1.438	Nil
s_3	0.889	9.4	1.651	4.5	1.271	0.2	1.135	Nil	1.171	0.4	...	..
Between open platens:												
p_1	0.984	Nil	1.674	3.2	1.278	Nil	...	..	...	..	...	..
Over-masticated	E1		E2		E3		E4		E5		E6	
Molded in press	0.980	..	1.730	..	1.285	..	1.145	..	1.185	..	1.446	..
In French chalk:												
f_1	...	..	...	..	...	..	...	..	...	..	1.244	14.0
f_2	...	..	1.733	Nil	1.274	0.9	1.141	0.4	1.169	1.5	1.148	20.6
In special mold:												
s_1	0.854	12.9	1.615	6.6	...	..	1.136	0.8	1.170	1.4	1.168	19.2
s_2	0.838	14.4	1.616	6.6	...	..	1.132	1.2	1.180	0.5	1.117	22.8
Between open platens:												
p_1	0.855	12.8	1.641	5.1	1.164	9.4	...	..	...	..	...	..

TABLE XI—EFFECT OF CHEMICAL TREATMENT OF RUBBER FOLLOWED BY NORMAL MASTICATION

Vulcanizing Treatment	F1		F2		F3		F4		F5		F6		F7	
	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.
Molded in press	0.977	..	0.984	..	0.974	..	0.969	..	0.980	..	0.983	..	1.002	..
In French chalk:														
f_1	...	..	...	..	...	..	...	..	0.984	Nil	...	..	...	..
f_2	...	..	...	..	...	..	...	..	0.976	0.4	0.980	0.3	0.997	0.5
Wrapped:														
w_1	0.980	Nil	...	..	...	..	0.974	Nil	0.982	Nil	0.986	Nil	0.995	0.7
w_3	0.980	Nil	...	..	...	..	...	..	0.985	Nil	0.972	1.1	0.982	2.0
In special mold:														
s_1	0.954	2.4	0.977	0.7	0.973	0.1	0.969	Nil	0.975	0.5	0.947	3.7	0.977	2.5
s_2	...	..	...	..	...	..	...	..	0.978	0.2	...	..	...	..
s_3	0.950	2.8	...	..	...	..	...	..	...	..	0.913	7.1	...	..
Between open platens:														
p_1	0.915	6.4	0.962	2.2	0.906	7.0	0.949	2.1	0.962	1.8	0.961	2.2	0.975	2.7
p_3	0.778	20.7	0.786	20.2	...	..	0.841	13.2	0.925	5.6	0.794	19.3	0.809	19.5

TABLE XII—EFFECT OF CHEMICAL TREATMENT OF RUBBER FOLLOWED BY OVER-MASTICATION

Vulcanizing Treatment	G1		G2		G3		G4		G5		G6	
	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.
Molded in press	0.978	..	0.978	..	0.974	..	0.974	..	0.990	..	0.977	..
In French chalk:												
f_1	0.970	0.8	...	..	...	..	0.965	0.9	0.972	1.8	...	..
f_2	...	..	...	..	...	..	0.943	3.2	0.957	3.3	0.745	23.7
Wrapped:												
w_1	...	..	0.952	2.6	...	..	0.938	3.7	0.993	Nil	...	..
w_3	...	..	...	..	...	..	0.941	3.4	0.964	2.7	0.829	14.8
In special mold:												
s_1	0.633	35.2	0.676	30.9	0.694	28.0	0.820	15.8	0.824	17.2	0.682	30.3
s_2	...	..	...	..	...	..	0.834	14.4	0.810	18.1	...	..
s_3	...	..	...	..	...	..	0.739	24.3	...	..	0.677	30.8
Between open platens:												
p_1	0.638	34.9	0.481	50.9	0.335	65.4	...	..	...	..	0.883	8.5
p_2	0.502	48.8	0.445	54.6	...	..	0.855	11.9	0.908	8.2	0.798	18.3

It was concluded that the treatments designed to oxidize the rubber or render it prone to oxidation, all gave rise to severe porosity, even when followed by only a short mastication (F1 to F3 and F6). The presence of Agerite Powder, during heat-treatment and mastication was of little value in resisting disaggregation and softening of the rubber, and the porosity was as severe in F6 as in F1. Softened rubber prepared by the Ungar-Schidrowitz process possessed a definite advantage over other rubbers brought to a similar plasticity by the special treatments F1

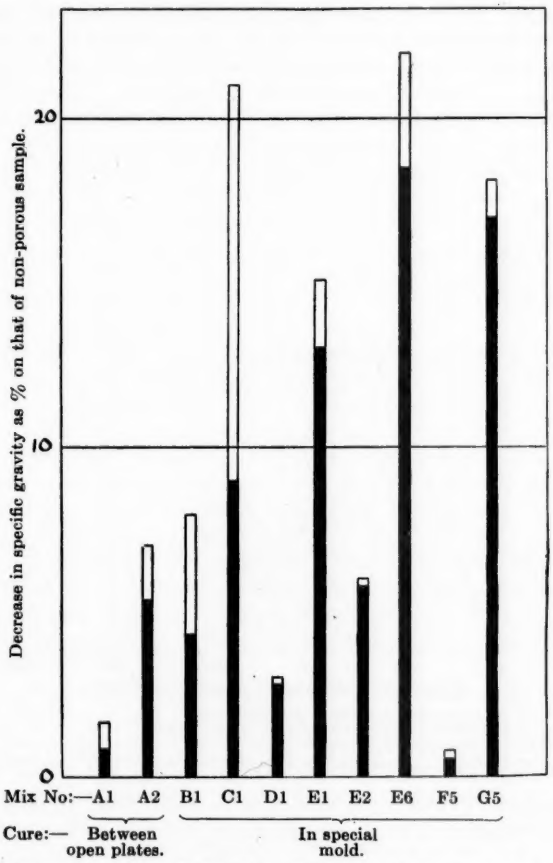
Decrease in specific gravity as % on that of non-porous sample.
20
10
0
Mix No:—A1 A2 B1 C1 D1 E1 E2 E6 F5 G5
Cure:— Between open plates.
In special mold.

Figure 7—Effect of Porosity of Sheeting from Even and Friction Speed Rolls

Shaded line - Even speed sheets.
Open line - Friction speed sheets.

to F3 or rubber killed on cold rolls G4; no porosity would be anticipated with this material under normal vulcanizing conditions. Mix G6, containing Agerite present during heat treatment and over-mastication, was slightly less prone to porosity than G1, which was similarly treated in the absence of antioxygen, whereas G5, containing antioxygen present during over-mastication, was no better than G4 similarly treated without Agerite. An anti-oxygen thus had no influence in

preventing the breakdown of rubber during mastication, and only slight action in preventing the oxidation of raw rubber exposed to heat.

These observations showed that porosity was increased by severe oxidation of the raw rubber and thus partially explained the production of porosity by excessive mastication, which is a similar oxidation process. The importance of purely physical factors, shown in earlier sections, indicated that oxygen was not liberated during vulcanization to produce porosity directly, but rather that the effect of the combined oxygen in softening the rubber, lead to increased entrapment of air during mastication. This air was only physically dissolved and was responsible for the rapid development of porosity in the early stages of vulcanization. A combination of oxidation and severe over-mastication on cold rolls gave the most serious porosity of any experienced in this investigation. The results confirmed that heat treatment or oxidation of raw rubber essentially reproduced the effects

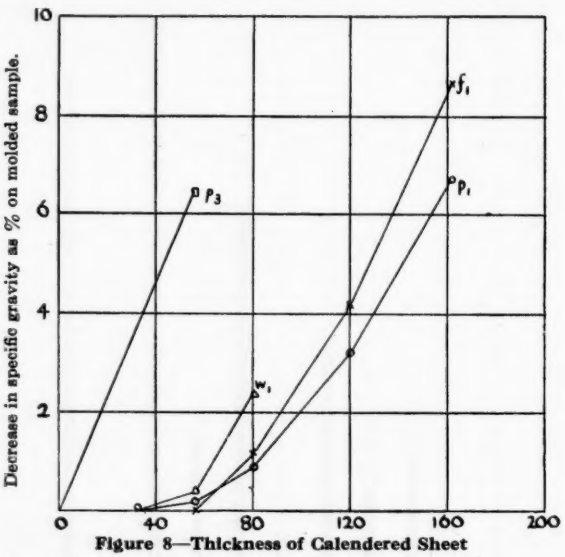

Figure 8—Thickness of Calendered Sheet

f_1 = Calendered and cured in French chalk.
p_1 = Calendered and cured between open platens.
w_1 = Calendered and wrapped.
p_3 = Calendered, moisture treated and cured between open platens.

of over-mastication; it was considered that in both cases, oxygen mainly acted catalytically in breaking down the structure of the raw rubber and so rendering it plastic.

Effect of Mechanical Treatment of the Mix.—During the course of this investigation of mixes prone to develop porosity, it became apparent that a number of factors in the mechanical treatment of the rubber stock had a direct influence on the degree of porosity produced. These factors are now considered in further detail.

Even and Friction Speeds of Rolls.—From results given in Fig. 7 it was evident that sheets run directly from the mill with the rolls set at friction speed, were slightly more liable to develop porosity than corresponding sheets calendered from even speed rolls. A possible explanation of this effect was that more gases were entrapped when the rolls were set at friction speed than when even speed, slower rolls were used; particularly if the sheet was passed through two nips.

Thickness of Calendered Sheet.—To investigate the effect of varying the thickness of the sheet, the base mix C1 made with over-masticated rubber, was calendered to a range of thicknesses from 16 to 160 mils. Samples of these sheets were cured in French chalk, wrapped and between open platens; the results of porosity measurements on the products are given in Fig. 8.

There was a steady increase in the porosity as the thickness of sheet was increased, and the author has observed the same effect of thickness in experiments on sponge rubbers. Wrapped samples or those vulcanized in French chalk, showed this influence of thickness rather more than samples cured between open platens. These results were explained by the fact that physically entrapped gases were liberated more easily at the surface of thin sheets and when the samples were freely exposed between open platens. As the thickness increased, a greater percentage of entrapped gas was retained in the sheet as pores during vulcanization.

Behavior of Plied Sheet.—Samples of the base mix B1, made with normally masticated rubber, were calendered to 16 mils, the surfaces were treated with French chalk, water or solvent naphtha and three layers of sheet, treated in each of these ways were plied together. The samples were vulcanized in the specially designed mold and the porosity was examined. The sheets treated with water or solvent showed slight porosity, owing to evaporation during cure. Chalked or unchalked sheets when plied together gave no sign of porosity, and were superior to sheet calendered directly to the resultant thickness.

Effect of Moisture.—The presence of moisture in rubber is a serious cause of porosity. There are numerous ways by which moisture may be present during vulcanization. In the first instance, it may be absorbed by the unvulcanized mix. As a general method of comparison, samples were immersed in water for 24 hours, the surfaces dried and the samples cured, together with corresponding dry mixes in the special mold and also between open platens. Results included in Tables VII and VIII (method of cure s_3 and w_3) showed that moisture increased porosity to a marked extent, even in stiff normally masticated mixes unlikely to become porous from other causes. In the second instance, moisture may be derived from the steam during vulcanization. Samples liable to develop porosity were cured in wet and dry French chalk; in a wrapper specially wetted or dried; with a long, slow rise and without a rise. The results of porosity measurements are given in Table XIII.

Porosity was generally increased by the use of wet chalk or wrapper, particularly when a long, slow rise was employed, as condensation from the steam probably occurred. The unvulcanized, soft rubber became saturated with moisture in the early stages of the rise and as the temperature increased, this was liberated as steam and porosity appeared.

Applications to Works Conditions

The first method of overcoming porosity problems in the works is the application of more pressure to the rubber during vulcanization. Thus, in the case of extruded cables, it may be necessary to lead-sheath the cable and strip the lead off again after vulcanization.

A soft mix must be avoided. This may be done by either adding stiffening fillers to the mix or reducing the degree of working which the rubber receives.

Adsorbed gas or moisture present in such a filler as carbon black must be removed, preferably by heating *in vacuo* before incorporating in rubber. Mastication at relatively high mill temperatures is an advantage, as moisture is largely removed and the rubber is not so severely softened.

With wrapped sheets, it is necessary to let the wrapper dry for some time before vulcanizing, to prevent the rubber from absorbing too much moisture during the early stages of the rise.

Porosity in open steam-cured products can sometimes be avoided by changing to a dry-cure process, even without applied pressure, as porosity due to moisture is prevented in the latter.

Trouble with porosity through direct calendering to a thick gage can be overcome by calendering through two nips to a thin sheet and plying together of the sheets.

Porosity in extruded products such as cables may sometimes be overcome by calendering and applying the sheet longitudinally.

Summary and Conclusions

A systematic investigation has been made of the factors likely to promote porosity in vulcanized rubber. Of the methods developed for assessing the degree of porosity, measurement of the percentage decrease in specific gravity is shown to be the most satisfactory. The permeability of the sheet to moisture, the acetone extraction of aged samples, and visual examination also give some indication of the degree of porosity.

Severe over-mastication, particularly on cold rolls, plasticizes rubber and increases the entrapment of gases during mixing. If the pressure applied during vulcanization is low, the volume decrease, which occurs as the rubber vulcanizes, causes further lowering of pressure; some of the entrapped gases are liberated, and as the rubber is partially set up free escape is prevented and pores are developed. The effect of over-mastication can also be produced by heat or oxidation treatment of the raw rubber.

Mechanical treatment of the mix, such as sheeting from the mill at friction speed, calendering to a thick gage, or extrusion of thick articles may increase the tendency for porosity under the appropriate conditions.

Softeners added to the mix produce the same effect as over-mastication in increasing porosity, whereas stiffening fillers oppose its production.

When no mechanical pressure is applied during vulcanization, porosity is likely to develop, but a slight pressure may cause even worse porosity through preventing the free escape of gases during the soft stage before vulcanization commences.

The degree of porosity depends on the conditions prevailing during the initial stages of vulcanization and is, in fact, a useful indication of setting up when scorching tests are being carried out. It is not influenced by the action of heat, in the later stages of vulcanization on the rubber-sulfur or oxygenated rubber complexes.

Moisture, derived from the ingredients of the mix, the processing or the methods of vulcanization, increases the porosity under appropriate conditions.

The use of ultra-accelerators or high-curing temperatures, tends to increase porosity of mixes liable to this defect, as the escaping gases are more completely entrapped by a rapid setting up of the rubber.

Some applications of the results to methods of overcoming porosity under works conditions are given.

In conclusion, the author wishes to express his appreciation to T. J. Drakeley and F. H. Cotton for their frequent suggestions and advice.

Table XIII

Effect of Moisture on Porosity

Treatment	Cure			B1 Normally Masticated		C1 Over-masticated		B4 Containing 10% Wax		B5 Containing 20% Wax		G6 Preheated and Over-masticated	
	Rise	Min. Cure	Steam Press. Lbs. per Sq. In.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.	S. G.	% Decr.
Molded in press	..	20	40	0.977	..	0.975	..	0.970	..	0.973	..	0.977	..
In chalk:													
Dry	5	30	40	0.970	0.7	0.970	0.5	0.964	0.6	0.967	0.6	...	..
Wet	5	30	40	0.971	0.6	0.964	1.1	0.962	0.8	.980	Nil	...	..
Dry	45	15	40	...	..	0.966	0.9	...	..	0.947	2.7	...	..
Wet	45	15	40	0.975	0.2	0.952	2.4	0.960	1.0	0.944	3.0	...	..
Wrapped:													
Damp cloth	5	30	40	0.978	Nil	0.968	0.7	0.957	1.3	0.957	1.7	...	..
Dry cloth	5	30	40	0.978	Nil	0.955	1.9	0.985	Nil	0.985	Nil	0.901	7.8
Wet cloth	45	15	40	0.969	0.8	0.967	0.8	0.980	Nil	0.980	Nil	0.829	15.1

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The Coating and Impregnation of Textiles with Latex

H. P. Stevens and W. H. Stevens

Of the various uses to which rubber latex might be expected to be applied, the textile industry is one of the more obvious, yet so far latex has been little used by the manufacturers of textiles, and relatively little work appears to have been done in this field of application. No doubt this arises from the fact that knowledge of the properties and handling of latex is not usually found among textile manufacturers. Where textiles impinge on rubber manufacture the conditions are otherwise, and the earliest application of latex to fibers is to be found in the manufacture of rubber goods.

Perhaps the first example of this application consists of the impregnation of tire cords with latex in the place of rubber sols, initiated and developed by the United States Rubber Company (British patent 178,811 (1921); 210,397 (1923)). No information is available as to the extent to which the latex treatment is carried on today, but it does not appear that such has become universal practice in spite of the advantages claimed by the inventors. There are no published data which enable a comparison of the advantages and disadvantages of latex impregnation to be made in comparison with the older process, but it is certain that the impregnation of textile fibers with latex is not as simple an operation as would appear at first sight.

Latex has also been used tentatively for proofing in the place of the usual rubber solvent doughs, but as far as information is available little progress has been made. It is hoped that those more closely identified with the rubber manufacturing industry will supply some information to complete these brief references to what has been done in this direction, as so very little has been published even in the form of patent specifications. Information being so scant and references so few, it was necessary to start at the beginning and to ascertain the behavior of textile fibers, in particular cotton in the presence of latex. This was particularly desirable because some statements have been made which seemed rather improbable.

The impression has been spread abroad that latex penetrates the fiber walls, the rubber in latex exhibiting an unexpected affinity for cellulose. The patent literature appears to be mainly responsible for these statements, and they require examination before we can proceed to describe our own work. British patent 178,811 describes the application of latex to what is termed an "unwoven warp-like element," with subsequent removal of moisture. The idea is to apply the latex to a number of cords running parallel between two rollers, the rollers being immersed in the latex. The cords must take up almost their own weight of latex, as the dry weight of the cord is increased 20–25 per cent. The latex available in those days would not be much over 30 per cent concentration. This can be understood; but the specification goes on to say that "microscopic tests on fibers subjected to latex treatment in this manner show a number of fibers in which the *rubber has penetrated* the lumen of the fiber" and later the specification refers to "increased penetration of the fibers by latex" apparently in contradistinction to the less efficient action of rubber sols. As far as the authors are aware, there has never been any publication by the inventors giving further details of the microscopic

examination to which they refer in their specification and explaining the method which they used. Their later patent (210,397) carries the matter no further, and merely deals with alternative methods for removal of moisture from the impregnated cords. It must be remembered that, at the time these patents were taken out, very little work had been done on the manipulation of latex and the manufacture of rubber goods therefrom. Consequently stabilizers, protective colloids, and wetting agents do not come into the picture. There is no mention of them in the patent literature of this period. Where expressions, such as "suitably prepared" latex and so forth, are met, it usually refers to the addition of ammonia. Subsequent to these patents various others appeared at intervals, but none of them theorizes on the reaction between or combination of rubber particles with the cellulose on the cell wall until eight or ten years later when there appeared British patents (338,381 (1929); 344,414 (1929)) dealing with improvement in the treatment of textiles with *inter alia* latex. The preamble of the former informs the public that it has already been proposed to impregnate spun or unspun fibers with rubber latex, and it is also known to impregnate threads, but the inventors claim a new process for the "impregnation of fibers." In the latter specification it is stated that the present invention results in "the unit fibers," being bound together with the material, *e. g.*, rubber latex with which they are impregnated, and later on that "the elementary fibers are deeply impregnated" when the invention is applied to twisted or cabled threads. These statements are repeated in the first claims. Similar statements are to be found in many other specifications, *e. g.*, British patent 325,916 (1928); the fibers or filaments are "individually impregnated" or British patent 338,381 (1929); when the latex is said to "coagulate, polymerize, or condense on the interior of the thread."

Now it is well known that, like rubber, cellulose is a rather inert substance of colloidal nature and indefinite constitution. Like rubber it reacts vigorously with only the most active of chemical reagents, but is at the same time liable to gradual changes which alter its physical properties with only slight modification of its chemical constitution. Such changes as these are slowly brought about by oxidizing agents, which may be cited as examples. The impregnation of one colloid by another is unlikely, for a colloidal membrane will hold back colloidally dissolved material while allowing crystalloids to pass. On the other hand, cellulose and rubber are different types of colloids. The former is normally hydrophyllic, the latter more readily takes up organic solvents. Rubber has also the power of absorbing moisture. It seems probable, however, that this results from the crystalloid and other impurities contained in raw rubber, as the purer the rubber the less the moisture absorbed. Moreover the absorption of moisture in excess of say 1 per cent results in a change from translucency or transparency to opacity, showing that the rubber has lost homogeneity. Hence, although from a theoretical standpoint, impregnation of cellulose by rubber from latex appears unlikely, it could not be altogether ruled out without investigation.

It should be possible to detect the presence of rubber in the fiber, particularly if it penetrated to the lumen. Experiments were, therefore, directed to microscopical observations of products obtained by the action of latex on cotton fibers. Hauser has already published work on these lines (*Metallgesellschaft Periodic Review*, January, 1931, No. 5) with colored photomicrographic illustrations of sections of cotton cords which have been impregnated with rubber solution or latex and subsequently treated with sulfuric acid to remove the cellulose, the rubber being discolored but not dissolved by this treatment. A perusal of Hauser's paper leaves some doubt as to the conclusion which the reader was intended to draw from the

results. The general impression seems to be that the latex particles penetrated neither the cell walls of the fibers nor even between the fibers forming the cord of a tire fabric.

Hauser's viewpoint is as follows: "A fabric previously soaked in a benzene rubber solution is already completely impregnated with rubber." "A fabric soaked in latex is only covered with an external coating of rubber," and from the photomicrograph it appears that, for instance, a single cord, latex treated, becomes surrounded with a layer of rubber and that the rubber particles contained in the latex have not even penetrated between the fibers which, twisted together, go to make up the cord. Presumably, however, rubber from a solution in benzene penetrates not only between the fibers forming the cord but also impregnates the fibers themselves, if indeed, that is what Hauser means by "complete impregnation" and "perfect impregnation."

From the size of the latex particle and the structure of the cotton fiber, it is very unlikely that the lumen of the latter could be filled with rubber as a result of latex treatment. It is also unlikely that this would result from treatment with a solution of rubber in benzene, for the cell walls of the fiber would not be permeable to rubber sols, and the fiber ends being closed there are no means of entrance to the capillary lumen. Hence it is more likely that by complete or perfect impregnation, Hauser had in mind merely penetration between the individual fibers of the cord and that the conclusion he formed was that such penetration could be effected by benzene sols of rubber but not by rubber latex particles. It was, therefore, resolved to repeat this work, using ordinary cotton threads.

Hauser's method of operation was not found very easy of control on account of the difficulty in manipulating the threads. However, Mr. F. Harris working in the authors' laboratory eventually succeeded in producing sections of latex impregnated thread. A photomicrograph of a section will be found in the *Rubber Growers' Association Bulletin* for December, 1933, in which the experimental work is shortly described. The conclusion arrived at was that latex particles showed no particular affinity for cotton cellulose, that they did not penetrate the fiber walls, and were not present in the lumen. In later experiments it was found that neither mercerization nor xanthation of the fiber walls availed to attach the rubber particles to the cellulose forming them.

The results, however, did show that the latex could, under suitable conditions, penetrate between the fibers composing the thread and did not merely form a layer of rubber round the outside of the thread, as is the case with the cord fabrics in Hauser's work. It would seem that under suitable conditions, and if the threads of the cord be not too tightly twisted, penetration of the latex between the fibers takes place. Obviously if the cord is very tightly twisted, the spaces between the individual fibers will be too small to permit the entrance of latex particles so that a filtration of the latex would take place, the serum being absorbed and the rubber particles left as a surface layer. That is exactly what happens if an attempt is made to impregnate unglazed porcelain or a piece of dry wood by immersion in latex. If then, latex is to find a use in textile factories, it can only be as a mechanical coating, binding, or finish; no special combination or reaction between cellulose and rubber can be anticipated which will result in a new product.

Lahey (British patent 337,359 (1929)) claims to obtain better "impregnation" of the fibers by mordanting with such substances as ammonium sulfate and tannates, but this seems very improbable.

The possibility of adapting latex to textiles may be roughly divided into two categories, namely, (1) filling or finishing, and (2) coating and, of course, combina-

tions of both. The first patent recorded (British patent 217,973 (1923)) dealing with the filling of textile fabrics with the aid of latex consists merely of a claim for the addition of latex to the usual filling and drying compositions. The inventors add the latex to the ordinary compositions, previously wet-ground. They do not make the mistake of adding the latex at an earlier stage. The compositions are applied to the fabric by known methods. The treated fabric may subsequently be acted on with coagulating agents and also vulcanized if desired. The text indicates the intension of using relatively small quantities of latex as the following examples show:

	(1) %	(2) %	(3) %
Farina	25	20–15	15
Latex	3	4	4
China clay	..	5–10	5
Water	72	71	66

It is stated that the addition of this small percentage of rubber latex renders the filling almost impervious to moisture, and that the treated fabric keeps its shape. It appears, therefore, that twelve years ago the idea of using latex as a binder for filler and pigments had already been experimentally developed, and it may be said to a degree which has not been much advanced in the intervening period.

Of other patents, reference may be made to the use of latex for "batting" fibers. This is a wet process, in which fibers are felted together to form a fibrous mass or sheet. It is suitable for wool, as the imbricated nature of the fiber interlocks adjacent fibers, but it cannot be applied to smooth fibers like cotton without a binder, and here latex has been found of use (British patent 232,763 (1924)). Little latex is said to be required, so that it should be well diluted before use and the product contains only 1–5 per cent of latex solids. The latex is not coagulated in the mass, but dries down to a gel. The product is quite porous, and no attempt is made to fill the interstices between the fibers with rubber. The product is, therefore, entirely different from a later invention (British patent 256,103 (1925)) in which an already felted material such as a felt sole is impregnated with latex. In this case the product is a non-porous solid rubber mass with interspaced, interlocked fibers and, therefore, a material of great strength.

There are among the patent specifications many other "new and improved processes," that is, according to the inventors, but most of these appear to deal with such modifications as might occur to anyone "skilled in the art" when working on the subject. Thus there are proposed variations in temperature and pressure; reduced pressure to remove the air from the interstices of the fabric and excess pressure to drive the latex in. In the later patents, by which time stabilizers and wetting agents for latex had become the usual practice, it is found that these are introduced in the patent specifications as novelties. In spread fabrics there are modifications in the machine, for instance, the tilt of the cloth leaving the roller, the location of the impregnating bath, and so forth. The spread fabric is dried on the usual steam chest or by festooning in hot air, previous to which the coating may be coagulated either by liquid or gaseous agents or alternatively flocculated latex may be used. The electrophoretic process may also be adapted to depositing rubber on fabric by passage over a former or roller acting as the anode. Similar discoveries which have been applied to the dipping process may be employed for fabrics. As an instance, the use of heat sensitized latex or one containing a dormant coagulant. An invention of greater interest (British patent 346,511 (1929); 403,121 (1932); 403,394 (1932)) deals with knitted fabrics such as stockings. These, after soaping,

are dyed and latex treated in one or more operations, the dye being fixed and the latex coagulated. The latex used is well diluted. The amount of rubber taken up is small and the effect is said to be indiscernible to the touch and imperceptible to the eye. Nevertheless, it is claimed that the wear and tear is improved, the tendency to "run" or "ladder" is reduced and the luster may also be diminished; all very valuable improvements.

There are various ways or modifications of the process of treating, or as it is termed "padding" a fabric with a latex composition. The rollers may be variously disposed. The latex composition may be brought up against the face of the cloth while passing round a roller; another roller in contact with the cloth revolves in the latex bath and carries the latex on the surface of the cloth. Alternatively the rollers may be immersed in the latex bath so that the cloth passes through the bath, and is therefore wetted on both sides. Comments have already been made on the behavior of latex in contact with a fine pored substance such as unglazed earthenware; the serum is absorbed and the latex particles left crowded on the surface. An action of this sort takes place to some extent with ordinary calico when padded by the first-mentioned process. A selective absorption ensues, less rubber is taken up than would be expected from the diminished volume of latex, and the latter undergoes concentration. Therefore in the experiments to be described the cloth was padded by leading it through a latex bath. The process may be repeated several times with the same length of cloth; each time a further quantity of latex composition is taken up. As a rule the number of pads does not exceed five. Bleached cloth readily takes up latex, but unbleached usually requires a suitable wetting agent. It should be noted that the cloth used throughout the experiments conformed to the following specification: warp, count 40, 72 ends to the inch; weft, count 64, 60 picks to the inch. The effect of a single padding through the latex is to give the cloth a "fuller" feel. This condition is not easily described, but is at once appreciated by those accustomed to handling cloth. It is a desirable property. The appearance and other properties of the cloth are not affected. After two or three paddings the cloth being dried between each, the rubber begins to become visible and can be felt when the cloth is handled. A textile man describes the feel as "tacky," though a rubber man would hardly do so, that is, unless the tacky feel was more pronounced. What may be described as the natural feel of a raw rubber surface is a defect from the textile viewpoint, and much of the work has been directed to the elucidation of this question. With every additional padding the tackiness increases. No doubt this arises from an increasing accumulation of non-rubber components from the latex, which as is well known are hygroscopic. Any selective absorption of serum solids tends to aggravate this condition, and cloth padded by surface contact with the latex composition is far more tacky than that obtained by thoroughly impregnating the cloth as, for instance, by soaking in latex and then expressing the excess by squeezing before drying. Hence one method of avoiding the tackiness is to arrange conditions of padding so that no selective absorption of serum components takes place. The serum substances can be leached out with warm water, and this treatment greatly improves the feel of the cloth. It is, however, a lengthy process and unsuitable for textile manufacture, at least for the majority of goods. If the latex be combined or compounded with other fillers the effect, as might be expected, is to reduce or to substantially remove the tack. Thus latex in combination with starches gives softer finishes, which are not tacky if the proportion of latex is kept low. In the course of this work a large number of substances were tried in combination with latex as finishes. These include mineral matter such as French chalk and China

clay, colloidal substances such as farina, soluble starch, feculose and dextrin, and also waxes. The usual methods were employed for the preparation of the baths, mineral substances being first wetted and then dispersed with a little casein, and when the substances such as soluble starch had an acid reaction this was first neutralized to prevent coagulation. In this way no difficulty was experienced on padding cloth with as many coats as desired. Usually two or three paddings sufficed. Where vulcanized rubber formed a component of the ultimate finish the latex was compounded with $1^1/_2$ per cent colloidal sulfur, 1 per cent colloidal zinc oxide, and 1 per cent sodium diethyl dithiocarbonate, all calculated on the dry rubber in the latex, vulcanization being effected in 20 minutes at 100° C.

When calendered, the cloth is smooth and glossy, quite attractive in appearance, and in every way satisfactory except for the tack, always noticeable when the proportion of rubber is relatively high. When vulcanizable latex is used to obtain a vulcanized finish, a similar tackiness was noted, but these samples showed an advantage after washing. As the resistance of a finish to such treatment is a very important property, a number of tests were made on a standard specification, namely, that drawn up by the Fastness Commission of the Chemistry of Dyeing and Textile Industries Section of the German Chemical Society. This briefly consists in boiling the sample for half an hour in a solution containing soap and sodium carbonate, after which it is allowed to cool and then alternately squeezed out and dipped ten times in the above solution. After thoroughly washing in cold water, it is allowed to dry and the loss in weight determined. This treatment is drastic enough to remove all but a trace of such soluble finishes as starch or dextrin and the bulk of a mineral filler held by them. As the amount of latex is increased in proportion to the fillers, the fastness is improved correspondingly, and with a combination in which rubber preponderates, very little filler is lost. Farina, soluble starch, and dextrin, which were investigated in some detail (see Tables I to IV, in which the figures are the averages of two or more determinations), it was found that the fastness was approximately proportional to the amount of rubber in the finish, so that the graphs, giving the proportion of rubber to the filler in the bath and the amounts of total filling removed are as nearly as possible straight lines. There are at present no data to indicate the composition of the material removed or retained; the amount of rubber removed is probably small. An analysis of the figures show that small proportions of rubber may be relatively advantageous. Thus with farina, the standard test removes the whole of the finish when farina is used alone, but with a mixture of latex and farina yielding a product containing approximately 60 per cent of farina and 40 per cent of rubber

TABLE I

LATEX-FARINA MIXTURES (UNVULCANIZED)

Composition of Finishing Mixture Used	% Dry Finish on Cotton Cloth	% Finish Removed by Washing, Calculated	
		(*a*) on the Cloth	(*b*) on the Finish
3 per cent farina	8	8	100
100 cc. 3 per cent farina, 3 cc. latex	12.3	7.6	72
100 cc. 3 per cent farina, 5 cc. latex	12.6	6.4	49
100 cc. 3 per cent farina, 10 cc. latex	14.8	4.4	30
100 cc. 3 per cent farina, 20 cc. latex	17.6	4.4	24
100 cc. 3 per cent farina, 30 cc. latex	20.3	4.0	11.9
100 cc. 3 per cent farina, 40 cc. latex	19.3	4.8	23
100 cc. 3 per cent farina, 50 cc. latex	27.7	4.4	19
Latex	32.8	2.3	7

TABLE II

LATEX-SOLUBLE STARCH MIXTURES (UNVULCANIZED)

Composition of Finishing Mixture Used	% Dry Finish on the Cloth	% Finish Removed by Washing, Calculated (a) on the Cloth	% Finish Removed by Washing, Calculated (b) on the Finish
30 per cent soluble starch	27.1	27.1	100
50 cc. 30 per cent soluble starch, 2.5 cc. latex	28.4	25.6	92.5
50 cc. 30 per cent soluble starch, 50 cc. latex	27.3	24.8	89
50 cc. 30 per cent soluble starch, 10 cc. latex	26.5	22.8	83.5
50 cc. 30 per cent soluble starch, 50 cc. latex	31.4	11.8	33.5
50 cc. 30 per cent soluble starch, 100 cc. latex	30.7	9.5	31
50 cc. 30 per cent soluble starch, 250 cc. latex	28.7	4.7	19.5
Latex	32.8	2.3	7

TABLE III

LATEX-SOLUBLE STARCH MIXTURES (VULCANIZED)

Composition of Finishing Mixture Used	% Dry Finish on the Cloth	% Finish Removed by Washing, Calculated (a) on the Cloth	% Finish Removed by Washing, Calculated (b) on the Finish
30 per cent soluble starch	27.1	27.1	100
50 cc. 30 per cent soluble starch, 2.5 cc. latex	27.5	26.5	98
50 cc. 30 per cent soluble starch, 5 cc. latex	27.4	26.5	96
50 cc. 30 per cent soluble starch, 10 cc. latex	29.4	21.9	74.5
50 cc. 40 per cent soluble starch, 50 cc. latex	32.8	15.7	48.5
50 cc. 30 per cent soluble starch, 100 cc. latex	35.1	11.4	30
50 cc. 30 per cent soluble starch, 250 cc. latex	34.9	9.5	27
Vulcanizable latex	34.3	2.3	6.8

TABLE IV

LATEX-WHITE DEXTRIN MIXTURES (UNVULCANIZED)

Composition of Finishing Mixture Used	% Dry Finish on the Cloth	% Finish Removed by Washing, Calculated (a) on the Cloth	% Finish Removed by Washing, Calculated (b) on the Finish
20 per cent dextrin	19.8	17.7	95
50 cc. 20 per cent dextrin, 5 cc. latex	25.4	21.0	80.6
50 cc. 20 per cent dextrin, 10 cc. latex	27.8	18.4	66
50 cc. 20 per cent dextrin, 20 cc. latex	30.8	16.5	53.5
50 cc. 20 per cent dextrin, 30 cc. latex	34.5	14.1	41
50 cc. 20 per cent dextrin, 40 cc. latex	34.9	11.9	39.3
50 cc. 20 per cent dextrin, 50 cc. latex	35.2	11.8	33.6
Latex	32.8	2.3	7

some 50 per cent is removed, a part of which may be rubber or at least the water-soluble ingredients of the latex. With high proportions of latex the amount of finish removed exceeds the farina present, while the rubber alone loses about 7 per cent. This roughly corresponds to the percentage of water-soluble components in whole-latex rubber. These conclusions are based on the assumption that the rubber and farina are taken up by the cloth in the proportions in which they exist in the bath. When padding with mixtures of latex and soluble starch, the effect of the latex is similar, some 50 per cent or a little less of the finish being removed when the bath consisted of about equal parts of rubber and starch. The use of vulcanizable latex with soluble starch showed no improvement on raw latex. When the quantity of starch was high, better results were obtained, that is, the

figures showed a higher proportion retained. With dextrin the results appear less favorable, but until it is known whether the components are taken up by the fabric in the same proportion in which they exist in the bath it is not possible to draw conclusions with certainty. All that can be said is that rubber, as latex, does not materially improve the retention of soluble carbohydrates by the cloth, and there is evidence indicating that when the carbohydrate is washed out part of the rubber may go too. Though vulcanized finishes behave very similarly to unvulcanized, and vulcanization does not improve the fastness to washing, it has one desirable effect—the cloth after soaping and washing is not tacky, as in the case of unvulcanized finishes.

Halogens rapidly attack rubber, and chlorinated rubbers are articles of commerce. The effect of treating a raw rubber surface with chlorine or bromine water is to produce a thin film of chlorinated or brominated product on the surface, so that these solutions can be used to remove tackiness from the surface of rubber. A number of experiments were made with dilute chlorine water with success. Three and one-half grams per liter of a solution having a p_H value of 1.4 as the minimum concentration was found to be effective in a two-minute treatment. The disadvantage is a slight yellowing of the surface, probably arising from a trace of iron in the latex. The treatment has little effect on the tensile strength. Bursting strain tests showed a loss of about 8 per cent, which is of the same order as that noted with other textile processes. The treatment can be applied to either vulcanized or unvulcanized finishes (see also British patent 415,195 (1933)). Quite a number of other methods have been tried to eliminate tackiness, but with little or no success. The subject is still engaging attention, as it appears to be fundamental. Textile experts say that it is the main drawback to the use of latex in finishes.

In connection with fastness to washing a number of experiments have been made with latex-China clay suspensions, and the results are set out in the accompanying Table V. As the percentage of clay increases the amount removed

TABLE V

Composition of Finish	% Dry Finish on Cotton Cloth	% Finish Removed by Washing, Calculated		
		(*a*) on the Cloth	(*b*) on the Finish	(*c*) after Allowing for Water Extractives
20 per cent rubber, 80 per cent China clay	45.7	5.6	12.4	8.3
30 per cent rubber, 70 per cent China clay	46.3	2.8	6.0	1.9
40 per cent rubber, 60 per cent China clay	45.7	2.3	5.1	1.0
50 per cent rubber, 50 per cent China clay	40.2	2.1	5.2	1.1
60 per cent rubber, 40 per cent China clay	42.5	1.9	4.8	0.7
80 per cent rubber, 20 per cent China clay	44.2	2.0	4.6	0.5
Latex (control)	42.6	1.7	4.1	...

also increases, as would be anticipated, but the amount of finish removed even with relatively high proportions of clay is quite small, and allowance must be made for the water extractives of the latex, which form a little over 4 per cent of the finish. The last column shows the percentage finish removed after allowing for these latex serum constituents. The figures are small and mostly almost negligible.

By treating cloth with wax, as for instance by padding with a wax emulsion, the cloth is rendered water repellant or "shower proof." A similar treatment of the cloth with latex has not this effect because, although a latex film has waterproofing

properties, especially if vulcanized, such a film is easily wetted. If, however, the cloth be padded with a mixture of a latex and wax emulsion certain advantages are obtained through the presence of the rubber and the water-repellant quality of the cloth is retained. In these experiments paraffin wax was emulsified by means of triethanolamine and stearic acid. The acid was added to the molten wax and the mixture poured into the triethanolamine in water, with constant stirring. After cooling, the resultant emulsion was mixed with latex in various proportions, as indicated by the accompanying tables, in which the amount of wax in the bath is given as a percentage of the dry rubber obtainable from the latex. The samples were obtained by padding three times in the mixture and drying the cloth between each padding. Smooth finishes were obtained. The wax tends to prevent the tackiness due to the rubber in the finish, and where the proportion of wax is double or more that of the rubber in the bath the surface of the finish is free from tackiness.

A drawback attached to the ordinary wax finish is the extraction of the wax in the dry cleaning process, so that the garment loses its show-proof qualities. Dry cleaners have to be prepared to retreat the garment after cleaning. It was found that the presence of vulcanized rubber in the finish retards or prevents the extraction of the wax, so that wax-rubber finishes should be free of the defect of the ordinary wax finishes. A series of wax-rubber finishes were therefore prepared with vulcanizable latex with different proportions of wax to rubber. After vulcanizing, the cloths were immersed in benzene for five minutes, after which they were removed and dried. After conditioning the samples of finished cloth were reweighed and the loss determined. This treatment was repeated until six determinations had been made on each sample of cloth. The results, the average of duplicate determinations are given in Table V. It will be noted that one part

TABLE VI

% Wax on Dry Rubber Content of Finishing Mixture	% Initial Dry Finishing Material Removed after 6 Successive Treatments with Benzene					
Pure wax finish	92	100	..	..	..	..
250	56	70.5	79.5	83	84	85
200	51	56.5	59.5	63.5	66.5	69.5
180	47.2	52.5	55.5	60	62.7	64
140	37.2	47.5	51.2	56.5	58.2	66.2
100	26	33.5	34.5	39	41.2	45.7
80	24.0	30.0	40.0	43.0	45.0	48.0
60	26	32.7	29.2	32.5	38	39.5
40	18.7	19.2	19.6	24.0	24.7	25.2
Pure latex finish	2.1	2.1	2.1	4.0	4.5	5.9

of rubber to two parts of wax causes a retention of about one-half the finish and with equal parts only, one-quarter of the finish is lost. The bulk of the samples retained their water-repellant properties after the whole six treatments. The dark line in the table divides those samples which have lost their water-repellant properties from the remainder. The former are confined to the pure wax finish and the two containing the largest properties of wax after two to four treatments. Very greatly improved fastness to benzene may therefore be said to result from the incorporation of vulcanizable latex with wax emulsion for finishing shower-proof cloth.

As petrol is largely used in dry cleaning processes, some further experiments were made in parallel with both benzene and petrol, using a limited number of

TABLE VII

% Paraffin Wax on Dry Rubber Content of Finishing Mixture	% Initial Dry Finishing Material Removed after Extraction in Benzene for		
Control	½ Hour	1 Hour	5 Hours
Vulcanized rubber	1.4	2.1	3.83
10	10.6	16.5	17.6
20	15.8	21.1	23.0
40	19.0	19.6	24.42

samples and prolonging the treatment. The samples were placed in a stoppered bottle with the cleaning agent and rotated about a horizontal axis for 0.5, 1, and 5 hours at a speed of 40 revolutions per minute. The accompanying Tables VII and VIII give the results.

TABLE VIII

% Parraffin Wax on Dry Rubber Content of Finishing Mixture	% Initial Dry Finishing Material Removed after Extraction in Petrol for		
Control	½ Hour	1 Hour	5 Hours
Vulcanized rubber	1.4	2.1	3.8
10	5.6	7.1	9.8
20	11.4	13.1	17.9
40	31.9	32.6	35.7

The figures do not run altogether proportionally, but if the extraction be sufficiently prolonged the petrol seems able to remove more of the finish than would be accounted for by the wax content alone. Again, there are at present no data to show that the wax and rubber are taken up by the cloth in the proportion in which they exist in the bath, though this may be assumed to be the case for the time being. The maximum treatment with solvent removed in most cases a quantity of the finish representing the extractable wax and the small amount of extractable rubber. Experiments were also made with beeswax and carnauba wax. The figures for beeswax are of a similar order to those for paraffin wax, but the carnauba wax is less firmly held and more of it is removed. This may be due to a difference in the degree of dispersion of the emulsion or suspensions originally used. Carnauba wax is more difficult to emulsify and is also less soluble in organic solvents.

Some experiments were also made to determine the influence of China clay in the same connection, the China clay being used in conjunction with latex and paraffin wax on the one hand and carnauba wax on the other. The figures for paraffin wax are given in Table IX and indicate an improvement, the amount of filling extracted after five hours being reduced to about one-third. A similar improvement was obtained in the case of carnauba wax.

TABLE IX

Composition of Finishing Mixture	% Initial Dry Finishing Material Removed by Extraction in Benzene for	
	1 Hour	5 Hours
40 per cent paraffin wax on the dry rubber content	19.6	23.52
40 per cent paraffin wax, 50 per cent China clay on the dry rubber content	10.8	10.6

A well known method of proofing consists in the application of an insoluble metallic soap formed in the cloth by first padding with a solution of sodium soap and subsequently with a solution of a metallic salt. This method should lend itself to the incorporation of latex by adding the latex to the soluble soaps, when the rubber should be coagulated and deposited with the insoluble metallic soap. To test this, cloth was padded six times with a 2 per cent sodium soap containing vulcanizable latex in various proportions, being dried between each padding and then placed in a 3 per cent solution of aluminium sulfate for two minutes. The cloth was then dried and the rubber vulcanized. Tests were then made by extraction with benzene. The figures are given in the accompanying Table X. The results were disappointing.

TABLE X

Ratio of Soap to Rubber in Padding Mixture	% Initial Dry Finishing Material Removed after Extraction in Benzene for	
	1 Hour	5 Hours
Pure soap	28.1	33.9
1:1	46	51.1
1:2	26.8	31.4
1:3	24.0	26.8
Pure rubber	2.1	3.8

Actually a finish of soap and rubber in equal parts showed a greater loss than soap alone, while two parts of rubber to one part of soap showed no advantage over soap alone. It may be that the conditions were not well chosen. If the soluble soap had been fully converted to insoluble soap it could hardly have increased the solubility of the rubber. It is rather to be supposed that the soluble soap was not completely decomposed, and therefore tended to render parts of the rubber soluble.

Some experimental work has also been done with spread mixes. The problem is simple, and no doubt the method is in use to some extent. The machinery employed is of a simple character, and from the general appearance of samples made with the textile appliances at the Department of Textile Chemistry of the Manchester College of Technology it may be concluded that the machines and appliances to be found in textile factories can be readily adapted to spreading compounded latex. No dough mills and such like plant are required, and consequently the manufacture of spread fabrics is not confined to rubber manufacturing plants. The rubber doughs used in the rubber trade are stiffer than latex mixtures; the latter therefore usually require thickening. This can be effected by the addition of viscous ingredients. Alternatively the latex may be flocculated. This considerably increases its bulk and stiffness; moreover the flocculated latex has less tendency to coagulate prematurely. Thickeners are substances such as caseinates, the various starches and chemical derivatives of same, dextrin, and so forth. Caseinates, particularly ammonium caseinate is very suitable, owing to its exceptional stabilizing powers with latex; 10 per cent on the rubber is a convenient proportion for compounding, and with care, finely ground pigments can be added direct without first wetting. Presumably, by suitable concentration after compounding, sufficiently stiff mixtures could be obtained with smaller proportions of thickeners, but no experiments made with less thickeners are here described. In all cases the latex mixture was made up and used direct. Table XI gives the weight of some white pigments which can be conveniently incorporated by means of 10 per cent of casein calculated on the dry rubber. It will be noted that very considerable loading is obtained in this way.

TABLE XI

Pigment	Wt. of Dry Pigment Compounded with 25 Cc. of Stabilized Latex Gm.	% Pigment on Dry Rubber Content of Latex
Lithopone	25	250
French chalk	27	270
China clay	21	210
Whiting	12	120

The next test indicated the increased weight obtained with four coats of the different pigments. The compounded latex does not strike through the cloth. The first coat is in all cases much heavier than subsequent coats, it is at least as heavy as the sum of the three subsequent ones. (Table XII.)

TABLE XII

Pigment	No. of Coats	% Increase in the Weight of the Cloth
China clay	1	55
	2	85
	3	89
	4	105
French chalk	1	66
	2	87
	3	108
	4	104
Lithopone	1	69
	2	100
	3	112
	4	119
Whiting*	1	54
	2	64
	3	73
	4	85

Vulcanizing ingredients may be incorporated with the latex. The amounts and proportions were the same as used in the finishing experiments already described, that is, 1.5 per cent sulfur, 1 per cent sodium diethyl dithiocarbonate, and 1 per cent of zinc oxide on the rubber, and vulcanization was effected in 20 minutes in air at 100° C. The only difference noted when using vulcanizable latex was an increase in viscosity due to the vulcanizing ingredients, so that the maximum amounts of fillers incorporated had to be reduced a little. (Table XIII.) Vulcanization also caused some slight discoloration of the coating.

TABLE XIII

Pigment	Wt. Compounded with 25 Cc. Latex Gm.	Wt. Compounded with 25 Cc. Vulcanizable Latex Gm.
Lithopone	25	24.2
French chalk	27	25
China clay	21	16
Whiting	12	11.5

Other thickeners tried successfully were the following:

Colloresin DK (methylated cellulose) in the proportion of 20 parts of a 5 per cent solution to 100 parts of latex, that is, 2.5 per cent of the dry rubber. Three hundred

and sixty parts of lithopone or 225 parts of China clay (on the rubber) were successfully incorporated with vulcanizable latex and spread on cloth. (Table XIV.)

TABLE XIV

Pigment	Wt. of Dry Pigment Compounded with 50 Cc. Stabilized Vulcanizable Latex Containing Colloresin DK Gm.	% Pigment on Dry Rubber Content of Latex
Lithopone	72	360
China clay	45	225

With gum tragasol, 250 cc. of 1 per cent solution were used per 100 parts of latex, that is, 6.5 per cent on the dry rubber. With a vulcanizing ingredient as before, 962 parts of lithopone or 537 parts of China clay (calculated on dry rubber) were incorporated, and the mixture was spread (Table XV).

TABLE XV

Pigment	Wt. of Dry Pigment Compounded with 20 Cc. Vulcanizable Latex Containing Gum Tragasol Gm.	% Pigment on Dry Rubber Content of Latex
Lithopone	77	962
China clay	43	537

A 7 per cent solution of farina was mixed with an equal volume of vulcanizable latex, that is, 17.5 per cent dry weight on the rubber, 350 parts of lithopone, or 200 parts of China clay were mixed and spread as above (Table XVI).

TABLE XVI

Pigment	Wt. of Dry Pigment Compounded with 50 Cc. Vulcanizable Latex Containing Farina Gm.	% Pigment on Dry Rubber Content of Latex
Lithopone	70	350
China clay	40	200

Colored pigment can of course be used, both as the common mineral pigments and as dye pastes, but care must be taken to avoid any components containing rubber oxidation catalysts. Thus, umber is unsuitable because it contains manganese. It is also possible to spread mixtures of latex and thickeners without fillers, but some have a tendency to tackiness, particularly with high proportions of rubber. Of those tried, namely colloresin, farina, and soluble starch, the last showed no tackiness. Either one or both sides of the cloth may be spread, and the products should find application as book cloths, waterproof aprons, light excluding cloth for photographic work, window blinds, etc.

Some work has been done to determine the aging properties of latex finishes and spread fabrics by the usual hot air oven aging process. It is obvious that, with so large a surface exposed, the conditions are more favorable to oxidation and consequent perishing than in the case of ordinary rubber goods. Consequently, the usual parallel drawn between hours in the oven at 70° C. and months' ordinary aging no longer apply, the oven aging being much more severe. No rules are as yet suggested or modified tests proposed.

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The Natural Stabilizers of Latex

W. H. Stevens

The paucity of information regarding the properties of natural rubber and allied latices, other than *Hevea Braziliensis*, is surprising. While great attention has been paid to fresh and preserved *Hevea* latex, little or nothing appears to have been done recently with other rubber or rubber-like (*e. g.*, gutta, balata, etc.) latices. Indeed, many authors of papers on rubber latex preface their articles with a statement that only *Hevea* latex will be considered, other latices being of no commercial interest.

It is likely, however, that a careful scientific examination of latices of botanical origin other than *Hevea* would yield much information of practical importance to the application of *Hevea* latex, although these latices may not be obtainable at present in commercial quantities. For instance, the fact that certain of these latices require no preservative indicates that they contain a natural stabilizer greatly superior to any substance occurring naturally in *Hevea* latex, or used in its industrial applications. The identification and application to *Hevea* of such natural stabilizers represents, therefore, an important technical research.

Though many references to latices other than *Hevea* are to be found in the literature, these are mostly somewhat old, and more often than not predate the advent of the rubber plantation industry, while more recently the attention so strongly focused on *Hevea* latex has caused the latices of other botanical origin to be entirely neglected.[1] The data given below for *Abiarana* gutta-percha latex may, therefore, be of some interest.

Acid Latex

It is well known that the charge on the rubber particles of preserved *Hevea* latex may be reversed, that is, the latex made acid. The change, however, is not very easy to bring about without causing flocculation, and ordinary preserved latex in this country requires a substantial addition of protective colloid, such as saponin, casein, hemoglobin, etc., in order to render it sufficiently stable for acidification. With fresh latex in which the natural protective colloid (protein) has not undergone alkaline hydrolysis the change is more readily brought about, and "acid zones" of definite p_H range have been identified.

Acid *Hevea* latex has already been carefully studied, as is evidenced by the patent literature,[2] and Twiss states that " . . . positively charged latex . . . has shown important advantages for certain applications."[3] When, however, ordinary protective colloids, such as those mentioned above, are employed, it is difficult to obtain acid latex of improved stability, although this is claimed in some cases.

From the following description of *Abiarana* latex, it will be realized that improved stability is not due to acidity as such, but to the particular protective colloids present, *e. g.*, certain proteins or allied substances, which are not precipitated under acidic conditions.

Abiarana Latex (Lucuma lastiocarpa)[4] Family Sapotacae Tribe Minusops

It would appear that although *Hevea* latex does not contain the best protein for maximum stability, the gutta-percha latex of the above resignation is nearer the mark. A sample received recently for examination and analysis was collected in Brazil, and sent home in a bottle without any preservative. It was received in per-

fectly good condition without signs of flocculation or local clotting. It had an acid reaction, and the p_H value increased slightly on continued storage to 4.0. It was not coagulated by alkalies, nor when these alkaline samples were again acidified. When mixed with ammonia-preserved *Hevea* latex and the mixture acidified, coagulation was not obtained, indicating that the stabilizing power was transferable. In an electrophoretic experiment deposition took place on the cathode.

Under the microscope the *Abiarana* latex showed active brownian movement, and appeared to resemble closely *Hevea* latex, though Freundlich has detected differences.[5] Macroscopically it exhibited rapid creaming, and formed a fairly clear serum with a small brownish sediment. The cream always appeared to be very thoroughly consolidated, but invariably redispersed completely on shaking without any signs of aggregation. This applied both to the latex as received, and after full dialysis.

The latex could be coagulated with acetone or alcohol, and the following analytical data were obtained.

	% on the Latex
Total solids	37.1
Crepe (by acetone, washed on rolls and dried)	33.6
Whence total solids excess	3.5
Diffusate (70 hours) by direct measurement	3.4
Specific gravity	0.984
Acetone extract of dry crepe	2.2
Nitrogen content of dry crepe	0.20
Gutta hydrocarbon (by difference)	31.2

The gutta separated by desiccation or coagulation was thermoplastic, softening readily in a 70° C. oven.

The distribution of the nitrogen was as follows:

	% on the Latex	% on the Dry Material
Total solids	0.33	0.89
Crepe	0.20	0.59
Diffusate	0.17	4.97

Since the sum of the nitrogen contents of the crepe and of the diffusate exceeds that of the total solids, it appears that some of the diffusable nitrogen is coagulated by the acetone and is not removed when the crepe is washed in water. It will also be noted that the acetone extract of the crepe is comparatively low for a gutta-percha (but this must not be ascribed to the use of acetone as coagulant as is evident from the figures).

To summarize. *Abiarana* latex closely resembles *Hevea* latex in many ways, but yet presents certain differences. Higher resin and protein contents might be expected in a gutta-percha latex, but what is unexpected is the marked qualitative difference in the natural stabilizer, presumably a protein or allied substance. Possibly the secret lies in the botanical origin of this interesting latex, for the bark of the species is said to be rich in tannins, which, no doubt, will contaminate the latex on tapping, and a tanned protein adsorption layer might be expected to be more stable to acid sera. Whatever the explanation this and similar latices merit fuller investigation, particularly from the viewpoint of the production of acid *Hevea* latex and its adaptation to useful purposes.

References

[1] Cf. "Technical Aspects of Emulsions" (Intern. Soc. of Leather Trades Chemists), **1935**, p. 123.

[2] British Patents 288,206, 288,268, 291,393, 300,394, 301,100, 301,805, 305,630, 306,747, 307,879, 307,912, 318,717, 324,663, 329,969, 331,563, 333,391, 334,581, 343,532, 350,106, 356,125, 367,183, 414,478, 421,519, 429,728.

[3] Twiss. J. Inst. Elec. Engineers, **75**, 485 (1934).

[4] "India-Rubber and Gutta-Percha," Seeligmann, Torrilhon, and Falconnet, **1903**, p. 304.

[5] Private communication.

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Determination of the Color of Latex

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It has long been felt that there is a need for a standard method of measuring the color of latex, a feature of the utmost commercial significance in determining its value and suitability for certain manufacturing processes. The method to be described is the direct outcome of a recent discussion with members of the scientific staff of the London Advisory Committee for Rubber Research.

Among the methods hitherto suggested for determining the color of latex are: (1) the use of standard tiles of varying tint with which the latex to be examined may be compared; (2) the use of a standard tintometer, such as that marketed under the trade name "Lovibond"; and (3) the employment of an apparatus embodying a photo-electric cell.

Whereas the first of these methods is simple, there is some difficulty in ensuring that the standard color-tiles shall always be of exactly the same tint, and that their density shall undergo no change whatever with time. The color of latex is so largely a neutral gray tint that it hardly seems necessary to employ the wide range of color values incorporated in a tintometer of the Lovibond type. Though a photo-electric cell should be capable of giving an accurate measure of the relative whiteness of different grades of latex, it would not measure differences in tint and its cost would probably prove prohibitive.

Considerations of Method.—The following considerations influenced the writer in developing the instrument and method later described.

The cleanest latex is devoid of color and appears a good white. Discolored latex is usually gray; it has no definite distinctive color, but fails to reflect as much white light as pure latex. On the other hand, some gray discolored latex exhibits a distinct yellow or brown tint, while other varieties appear slightly blue. The grayness of preserved latex is usually produced by ferrous sulfide in a finely dispersed condition (see Rhodes and Sekar, *India Rubber J.*, **87**, 586 (1934)). It seems that when completely present as ferrous sulfide, iron gives to latex a slightly blue-gray tint, while when the sulfide is oxidized it produces ferric hydroxide (by action with the ammonia present), and this imparts a brownish or yellow tinge to latex. As the color of latex is mainly the result of lowered reflective capacity, it was considered that a photometer method might with advantage be employed to measure the "degree of whiteness."

Preliminary experiments demonstrated clearly that slight differences in the tint of latices render it difficult for the eye to compare the whiteness or "brightness" of one with the other, or of either with a standard. At the same time, the relative reflecting power of latices are of greater commercial significance than their actual color; experiments were therefore made with a view to determining the relative brightness of latices when viewed through color screens which masked any difference which existed between the tint of the latices concerned.

It was borne in mind that a method to be generally adopted must be simple and the apparatus required inexpensive.

The method finally adopted should be such that the results obtained by different people should be the same, despite the variation in color-sensitiveness of individual eyes.

The standard of whiteness or brightness chosen should be of a type readily available throughout the world, and should be of a nature which renders cleaning easy. It was thought doubtful whether the usual standards, such as magnesium oxide and magnesium carbonate, would fulfil these requirements.

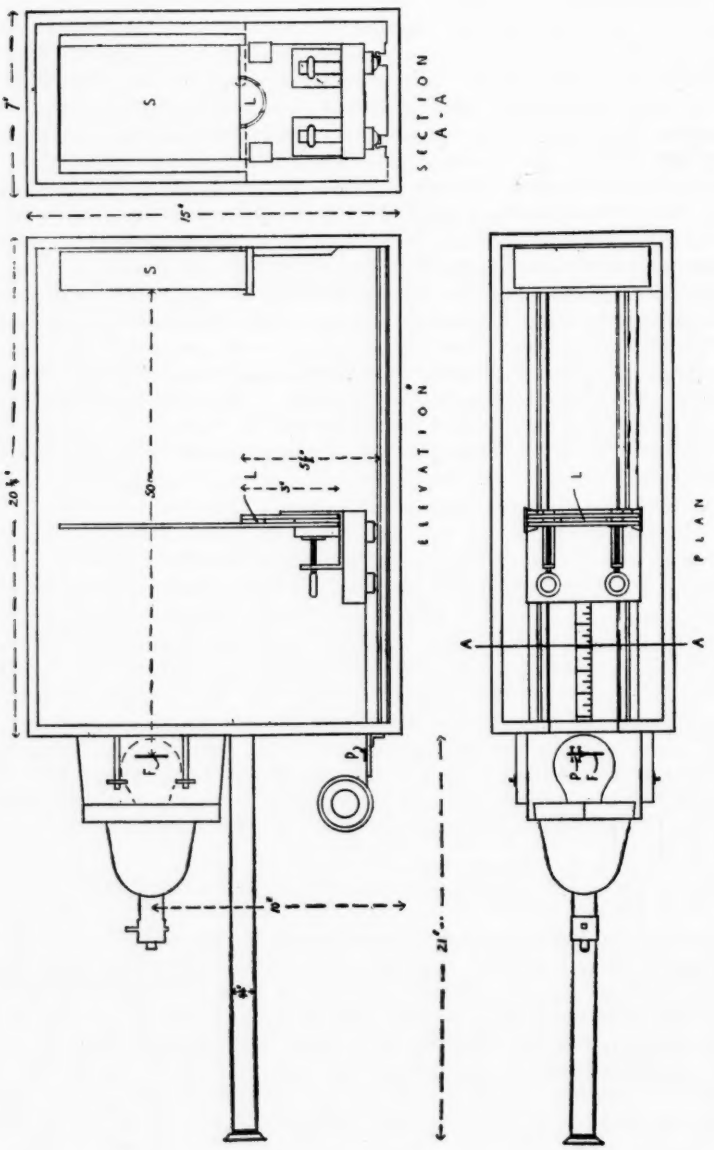
Description of Apparatus.—The apparatus finally developed is shown in sectional elevation, end elevation, and plan in the accompanying diagram. It consists essentially of a box 52.5 cm. (= $20^3/_4$ in.) long, 38 cm. (= 15 in.) high by 17.7 cm. (= 7 in.) wide, fitted with a light-tight door which could easily be opened. Along the bottom of the inside of the box run two rails, upon which is mounted a small oak carriage on the lower surface of which are fixed four ball-bearing runners, which constrain it to move along the rails. Suitable screw clamps on this carriage serve to hold in a vertical plane a special latex cell L, made by clamping together two sheets of 21-oz. glass, between which are interposed pieces of vulcanized rubber cut by means of a Schopper ring punch from a disc 3 mm. thick.

At the left-hand end of the box, above the level of the latex cell, is fitted a lamp-house designed to allow horizontal movement of a one-half-watt type gas-filled metal filament lamp (clear glass type; the opal bulbs are not so suitable) which shines through a hole in the end of the box and illuminates the latex in the cell and also the standard of whiteness, namely, a block of domestic cooking salt, $1^1/_2$ in. thick, standing on a small shelf at the further end of the box. The position of the lamp is adjusted until the distance between the filament and the surface of the block of salt is 50 cm.

Below the lamp is fixed a horizontal sight-tube or collimator 21 in. in length, which just passes through the left-hand end of the box. The center line of this tube is level with the top of the lower glass plate of the latex cell.

A flexible steel rule divided in centimeters is fastened to the lower side of the cell-carriage in such a manner that its zero end comes vertically under the surface of the latex illuminated by the lamp. The scale protrudes through the left-hand end of the box so that the horizontal distance between the latex cell and the filament of the lamp may be read from the pointer P, which can be adjusted so that it is vertically below the incandescent filament. The flexible steel tape forms a convenient means whereby the carriage may be moved backwards or forwards along the rails from outside the box by the observer situated at the eye-piece end of the collimator. It is convenient to have the external end of the steel rule coiled in a reel so that it shall not inconvenience the observer. The inside of the box is painted a dull black.

Method of Use.—The movable carriage is first pushed along the rails to the right-hand end of the box, when it can be easily lifted and removed from the open door and stood on the table or other support outside the apparatus. The steel rule, being flexible, will allow this. The latex cell is then built up by placing the larger glass plate (10 in. by 5 in.) horizontally on the table, putting the semi-circular piece of rubber in the position shown in the drawing so that its ends are on a line parallel and 3 in. from the lower end of the plate, arranging the other three rubber distance pieces so that they will take the pressure of the spring paper clips used to hold the cell together, and finally covering it with the smaller glass plate (5 in. by 3 in.), so that one of its longer edges is level with the top of the semi-circular cell. The two glass plates are then clamped together by means of three spring paper clips. The cell is then fixed in a vertical position on the extreme right-hand edge of the carriage as shown in the diagram. The semi-circular cell formed by the rubber half-ring is then carefully filled with the latex under investigation by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means of a 5-cc. pipette. The upper surface of the latex must coincide with the top of the shorter glass plate.

The carriage is then replaced on the rails, the door closed, and the lamp F switched on. On looking through the tube T, the field of view, restricted to what can be seen through the further end of the tube, will be found to be bisected by the upper surface of the latex in the cell into two semi-circular areas, the relative brightness of which will alter as the carriage is moved backwards and forwards on the rails by means of the protruding end of the flexible steel rule. It will be noticed that the light from the lamp has to go twice through the larger sheet of glass in passing to the block of salt or other standard of whiteness, and back to the eye-piece; and it also has to go twice through the same piece of glass in reflection from the surface of the latex in the cell. Any slight color of the glass will, therefore, not interfere with the relative brightness of the latex and the white standard. The filament of the lamp has been placed a few centimeters above the center line of the collimator, because it was found during preliminary experiments that, when on the same level as the surface of the latex in the cell, an image of the filament in the sheet of glass came within the field of vision and vitiated the result. It is suggested that the vertical distance between the center of the circular filament and the surface of the latex in the cell should be standardized at that indicated in the drawing (3 in.).

With white and neutral gray latices, it has been found possible to match the brightness of the white standard with that of the latex by moving the latex cell backwards and forwards, while looking through the tube. If brightness and whiteness be considered as synonymous terms:

$$\frac{\text{Whiteness of latex}}{\text{Standard of white}} = \frac{(\text{Distance from filament to latex})^2}{(\text{Distance from filament to salt})^2} = \frac{(\text{Steel tape reading})^2}{(50)^2}$$

In the above equation the slight error introduced through the electric lamp being above the level of the latex has been neglected; this is justifiable if the vertical distance between the axis of the lamp and the surface of the latex be standardized (*e. g.*, at 3 in.).

It is suggested that although the brightness of an illuminated surface actually varies inversely as the square of the distance from the light source, it would be sufficient from a practical point of view to give a sample of latex a brightness or whiteness index equal to the reading of this instrument when balanced against the brightness of the standard white surface situated at a distance 50 cm. from the filament.

With latices showing color in addition to neutral grayness, it was found that the use of an eye-piece containing a disc of Wratten gelatin color filter on the end of the collimator completely masked any difference between the tint of the latex and the salt, thus rendering it easy to obtain a balance. Usually the reading with an orange or red filter was slightly higher than that obtained employing a blue filter, because most of the samples of latex tested had a slight yellow tinge. So-called blue latex is almost a neutral gray.

Results.—The first tests made with the new instrument were on a particularly white sample of latex supplied by the London Advisory Committee for Rubber Research. A block of Weston's salt was used as a standard of whiteness and the illuminant was a 150-watt gas-filled half-watt type lamp with clear glass, which enabled the position of the filament to be determined accurately. The distance from the filament to the surface of the salt was adjusted to 50 cm.

The first readings were taken without the use of a color filter. Ten separate measurements were made, the position of the latex carriage being altered at the

end of each determination so that a fresh balance had to be obtained. The readings are given in the first column of Table I.

TABLE I

Results of a determination of the color of a particularly white sample of latex, A, supplied by the Ceylon Rubber Research Scheme.

Standard white — a block of Weston's salt
Illuminant — 150 watt gas-filled clear-glass Osram electric lamp
Distance from lamp filament to salt = 50 cm.

READINGS IN CM. FROM FILAMENT TO LATEX AT BALANCE

Without Color Filter	Deviation from Mean	Orange Filter	Deviation from Mean	Blue Filter	Deviation from Mean
42.0	0.7	40.4	0.8	40.5	0.4
40.8	0.5	42.4	1.2	40.3	0.6
41.6	0.3	41.0	0.2	41.4	0.5
42.1	0.8	40.9	0.3	40.9	0.0
40.7	0.6	41.1	0.1	41.3	0.4
40.2	1.1	..	...	..	...
42.1	0.8	..	...	..	...
42.4	1.1	..	...	..	...
40.5	0.8	..	...	..	...
40.2	1.1	..	...	..	...
Mean = 41.26	Average Deviation 0.78	Mean = 41.16	Average Deviation 0.52	Mean = 40.88	Average Deviation 0.38

A Wratten orange gelatin filter was then placed in front of the eye-piece, and the process of balancing the brightness of the latex against that of the salt was repeated a further five times. The results are given in the second column of Table I; and the average deviation of these readings from the mean was considerably less than when not using a filter. The tests were then repeated with a Wratten blue filter; again the deviation of the individual readings from the mean of the five was much less than when no filter was employed. It was found far more easy to decide when a balance had been reached with a color screen in front of the eye-piece; with many latices subsequently tested it was impossible to obtain a balance without interposing a color screen to mask differences between the tints of the latex and the standard. It was therefore decided in all further determinations to work only with color screens in the eye-piece.

Effect of Changing Salt Used as Standard White.—Several sets of readings were taken on the same latex, using salt blocks of different manufacture. When taking the readings given in Table I a block of Weston's salt was employed. Table II

TABLE II

Repeat determination of color of latex A, using a block of "Greatham" salt in place of Weston's salt as standard. Other conditions as in Table I.

READINGS IN CM. FROM FILAMENT TO LATEX AT BALANCE

Without Color Filter	Deviation from Mean	Orange Filter	Deviation from Mean	Blue Filter	Deviation from Mean
40.0	0.7	40.0	0.7	41.8	0.7
38.9	0.4	31.4	0.7	41.3	0.2
38.1	1.2	40.4	0.3	41.4	0.3
39.7	0.4	41.5	0.8	40.6	0.5
39.6	0.3	40.4	0.3	40.4	0.7
Mean = 39.3	Average Deviation 0.60	Mean = 40.7	Average Deviation 0.56	Mean = 41.1	Average Deviation 0.48

gives the results obtained on the same white latex using a block of Greatham salt (supplied by the producers of Cerebos). It will be noticed that the readings taken without a filter, and those taken through an orange filter were slightly lower in the case of the Greatham salt, suggesting that this was slightly whiter or more highly reflecting than the Weston's salt. Several samples of commercial domestic salt were tested, but the differences noted were well within the limits of experimental error, suggested by the average deviation from the mean readings indicated in Tables I and II, etc. In all the later work a block of Greatham salt was employed, as this seemed relatively whiter and should be easily obtainable.

Yellow and Blue Latices.—Tables III, IV, and X give results obtained on samples of latex which were definitely yellow or yellow-gray in appearance. In each case the index for yellow as indicated by the reading at balance when employing an orange filter was appreciably higher than the reading given when using a blue filter. This was a clear indication that the latex was reflecting more yellow light than blue light; hence the reason for its appearing yellow in tint. Tables V and VI refer to latices which appeared neutral gray; in these cases the mean readings for blue and orange are almost identical. The eye was not sensitive to slight changes in brightness of the latex when viewed through a Wratten red filter, and therefore in later work only the orange and blue filters were used. The latex used for the tests reported in Table II might be described as a blue-gray latex. In this instance the index figure for blue is slightly above that for orange.

TABLE III

Determination of color of a 23-months' old sample of off-colored yellow latex, B, supplied by the Ceylon Rubber Research Scheme (sediment not stirred in before test). Greatham salt employed as white standard. 150 watt Osram lamp. Note higher reading for orange than blue.

READINGS IN CM. FROM FILAMENT TO LATEX AT BALANCE

Orange Filter	Deviation from Mean	Blue Filter	Deviation from Mean
35.8	0.8	30.5	0.0
35.1	0.1	30.2	0.3
35.1	0.1	31.1	0.6
34.5	0.5	31.3	0.2
34.4	0.6	30.3	0.2
Mean = 35.0	Average Deviation 0.42	Mean = 30.5	Average Deviation 0.26

Eye-Fatigue.—It soon became apparent that the eye rapidly fatigued during this type of test. After obtaining the first balance between the brightness of the latex and that of the salt (with or without color filter interposed), increasing difficulty was experienced in being certain that subsequent balances were correct. Often after the observer has moved the latex-cell into a position at which the brightness of the two halves of the field of view appears equal, either the latex or the salt may suddenly appear darker. At times the brightness of the upper and lower halves may appear to alternate, and an optical illusion of flickering is experienced. The eyes of various investigators fatigued at different rates, and some found considerable difficulty in matching the brightness of the two halves of the field after two or three tests.

In order to reduce errors caused by eye-fatigue, it was decided to obtain a balance five times by drawing the latex-carriage slowly towards the lamp from a position

in which the latex appeared too dark, followed by five times in which the cell was pushed slowly from near the lamp towards the salt; the mean of the ten readings to be taken as the true reading. As shown in Table V, the average of the second five readings was usually different from those of the first five, but the deviation from the mean of the five was generally lower than the deviation of the individual readings given in Tables I, II, III and IV from their mean.

TABLE IV

Selected results from tests on color of slightly yellow latex, C, supplied by Rubber Research Scheme (sediment not stirred in). Conditions as in Table III.

Blue Filter						Orange Filter			
Readings by F. H. C.	Deviation from Mean	Independent Observer	Deviation from Mean	Readings by F. H. C. (Unsystematic)	Deviation from Mean	Readings when Balance Reached from Latex too Dark (F. H. C.)	Deviation from Mean	Readings when Balance Reached from Latex too Light (F. H. C.)	Deviation from Mean
37.2	0.7	34.4	2.4	41.1	0.2	41.7	0.1	38.7	0.1
38.2	0.3	36.9	0.1	40.6	0.3	41.5	0.1	38.5	0.3
38.7	0.8	36.8	0.0	41.9	1.0	41.5	0.1	39.0	0.2
38.6	0.7	37.7	0.9	39.7	1.2	42.2	0.6	39.0	0.2
37.0	0.9	38.3	1.5	41.3	0.4	41.3	0.3	38.8	0.0
Mean = 37.9	Average Deviation 0.68	Mean = 36.8	Average Deviation 0.98	Mean = 40.9	Average Deviation 0.62	Mean = 41.6	Average Deviation 0.24	Mean = 38.8	Average Deviation 0.16

Mean reading with blue filter = 37.4 cm. Mean reading with orange filter = 40.2 cm.

TABLE V

Determinations of color of a sample of "Fair Color" latex obtained on the market. The latex, which was slightly gray, was shaken before testing, to disperse sediment. Greatham salt used as a white standard. Readings taken by the author and an independent observer.

Red filter = Wratten gelatin color filter. Series 29.
Blue filter = Wratten gelatin color filter. Series 48.
Orange filter = Wratten gelatin color filter. Series 22.

Balance Approached from:	Readings by F. H. C.			Independent Observer		
	Red	Blue	Orange	Red	Blue	Orange
Latex too dark	37.5	40.1	40.0	36.9	39.4	38.7
	37.5	40.2	39.3	36.2	37.2	38.8
	37.8	49.0	39.4	35.8	39.7	39.0
	38.4	40.0	38.8	37.2	38.9	40.5
	37.8	39.3	38.4	38.5	38.2	40.0
	39.5	37.3	38.0	33.8	38.0	41.6
Latex too light	36.8	37.5	39.5	33.7	35.0	38.0
	38.5	37.5	38.1	33.2	33.5	36.5
	37.5	36.5	36.8	34.2	36.5	38.7
	36.8	37.0	39.3	34.7	38.5	35.4
	Red	Blue	Orange	Red	Blue	Orange
Means:	37.8	38.6	38.8	35.4	37.5	38.7

It was later considered more rational, in eliminating the effects of eye-fatigue on the upper and lower half of the retina, to standardize a method in which the balance was attained alternately from the latex being darker and lighter than the standard. This method was found satisfactory (see Tables VI–XI).

TABLE VI

Sample of gray latex considered on market as of "bad color." Shaken to disperse sediment before testing. 150-watt lamp; Greatham salt as standard. Readings marked "D" were obtained by moving latex-cell from a position where it appeared too dark; those marked "L," from a position in which the latex was lighter than the standard.

Balance Approached from:	Readings by F. H. C.			Independent Observer		
	Red	Blue	Orange	Red	Blue	Orange
D	37.2	39.2	36.5	34.6	36.6	34.9
L	35.1	35.2	36.5	33.0	34.4	37.6
D	36.2	37.5	37.3	33.7	35.8	35.2
L	34.1	36.3	36.8	34.8	33.8	38.4
D	39.2	38.0	36.8	35.2	36.9	37.5
L	34.2	36.0	36.0	35.7	36.3	36.0
D	36.8	37.8	37.5	36.1	37.6	36.3
L	35.5	36.2	37.2	37.0	35.8	34.0
D	37.0	37.1	38.0	35.8	37.2	37.3
L	36.5	35.5	36.7	35.0	36.8	36.3
	Red	Blue	Orange	Red	Blue	Orange
Means:	36.2	36.9	36.9	35.4	36.1	36.4

TABLE VII

Repeat determinations by different observers (through an orange filter) of the brightness of a "poor color" gray latex found by the author in his original tests to give readings: red, 35.5; orange, 36.8; blue, 36.27.

Each of the readings given below is the mean of ten determinations in which the balance was attained alternately from too dark and too light.

Observer	Remarks	Mean of 10 Readings
F. H. C.		36.8
F. H. C.		36.8
F. H. C.	Using small aperture eye-piece	37.0
S.		34.3
S.	Using small aperture eye-piece	34.7
P.		33.7
B. L. D.		33.3
B. L. D.	Using small aperture eye-piece	34.8
R. K.	Very weak eyes	34.0

TABLE VIII

Results of color tests on a sample of "Jatex" 60 per cent concentrated latex: (*a*) using 150-watt gas-filled clear-glass Osram lamp; (*b*) using 40-watt gas-filled clear-glass lamp as illuminant. The latter lamp was much smaller, and the holder had to be shifted in order to bring the filament into a position approximately 50 cm. from the salt.

Balance Approached from	Using 150-Watt Lamp			Using 40-Watt Lamp		
	Orange	Red	Blue	Orange	Red	Blue
D	37.4	39.8	38.8	40.5	39.2	34.9
L	37.5	37.6	36.1	41.9	37.0	43.5
D	39.0	39.5	38.5	39.8	37.9	39.8
L	37.8	37.1	39.6	39.5	40.1	40.8
D	37.7	38.5	40.9	41.9	36.9	38.9
L	38.2	38.2	38.2	38.9	36.4	40.3
D	38.8	37.5	29.2	38.0	38.2	40.0
L	39.3	37.5	38.8	38.7	36.5	39.8
D	38.7	38.6	39.8	38.9	37.3	40.3
L	38.9	37.3	38.0	41.1	36.3	39.2
Means:	38.3	38.2	38.6	39.9	37.6	40.8
Maximum variations	1.9	2.7	4.8	3.9	3.8	6.0

TABLE IX

Repeat determinations of the color of white latex, A (compare Tables I and II), using 150-watt lamp and Greatham salt as standard. In the tests summarized in this Table, the balance was reached alternately from the latex appearing too dark and too light. In order to allow for the different sensitivity of the upper and lower halves of the retina, sets of ten readings were taken for each color, with and without a glass prism which inverted the field of view. In the table below, "P" indicates that the readings in the column were taken with the inverting prism before the eye-piece.

	Red	P	Orange	P	Blue	P
Mean of 10 readings	41.83	41.45	41.73	38.98	39.28	39.40
Average deviation from mean	1.67	0.41	0.83	0.78	0.68	0.80
Maximum variation	6.4	2.1	3.5	3.4	2.0	3.2
Mean of readings with and without prism	41.64		40.36		39.34	

TABLE X

Summary of two separate sets of determinations of the color of a yellow-gray off-colored latex. These sets of determinations were made several days apart, when the observer was tired—the first being carried out late in the evening.

Each set of color determinations included ten readings taken with the inverting prism in front of the eye-piece. The object of the tests was to find how the means of readings taken at one time would compare with those taken under different circumstances—particularly when the investigator was tired—at another time.

		Orange	P	Blue	P
First series of determinations	Mean of 10 readings	34.07	31.95	31.99	30.51
	Average deviation from mean	1.19	1.49	0.65	0.91
	Maximum variation	6.7	5.7	2.5	3.1
	Mean of readings with and without prism	33.01		31.25	
			P		P
Second series of determinations	Mean of 10 readings	32.68	33.90	31.02	31.40
	Average deviation from mean	0.64	0.56	0.71	0.52
	Maximum variation	2.5	2.3	3.2	2.1
	Mean of readings with and without prism	33.29		31.21	

TABLE XI

Summary of results of determinations of color of "very bad colored" gray latex obtained on market: (*a*) using Greatham salt block as standard white; (*b*) using freshly deposited magnesium oxide as white standard.

Readings in columns headed "P" were taken with an inverting prism in front of the eye-piece.

		Orange	P	Blue	P
Using common salt as white standard	Mean of 10 readings	33.33	31.72	34.73	33.92
	Average deviation from mean	0.47	0.40	0.61	0.66
	Maximum variation	1.5	1.5	2.2	2.7
	Mean of readings with and without prism	32.53		34.33	

			P		P
Using magnesium oxide as white standard	Mean of 10 readings	31.56	31.16	32.26	31.29
	Average deviation from mean	0.81	0.60	0.66	0.63
	Maximum variation	3.1	2.3	2.2	2.4
	Mean of readings with and without prism	31.36		31.78	

Effect of Candle-power of Illuminant.—Theoretically the candle-power of the lamp should not affect the relative brightness, but it was thought wise to test this in practice. Table VIII shows the results of a series of tests on a sample of Jatex 60 per cent, centrifuged concentrated latex, using Wratten orange, red, and blue filters, respectively, employing a 150-watt gas-filled clear-glass Osram lamp in the first case and a 40-watt clear-glass, gas-filled lamp in the second case. The illumination with the low power bulb was so poor that difficulty was experienced in deciding when a balance was reached. The figures obtained are not identical, but the readings for orange, red, and blue are in the same order of magnitude in each case. A 40-watt lamp does not give sufficient illumination for routine testing, as the maximum variations between readings for individual color filters were greater with the 40-watt lamp than with the 150-watt illuminant (see Table VIII).

Use of Inverting Prism.—The fact that different observers did not always obtain the same mean readings of the color of a sample of latex when viewed through a particular color screen (see Table VII), though the readings of each individual observer were usually consistent among themselves, suggested that possibly the upper and lower halves of the retina of the eye are not necessarily equally sensitive to color. It seemed that in no other way could be explained the type of result of which Table VII gives a summary. It was therefore decided to try the effect of taking readings when the brightness of the latex was balanced against that of the standard, and then when an inverting prism was placed in front of the eye-piece. An optical prism taken from a pair of field glasses was found to be admirably suitable for the purpose; it could be held in such a position that it caused the latex to appear in the upper half of the field of view. The eye naturally looked at the line produced by the upper surface of the latex which bisected the field of view. As shown in Tables IX, X, and XI, the readings obtained with the inverting prism in position were often appreciably different from those obtained in the normal way, though consistent among themselves. The average deviation from the mean of ten readings taken with the prism and the maximum variation between these readings was in no case higher than might have been obtained without the prism, though the average of the readings with the prism was in some cases nearly 3 cm. above or below those without the prism.

It was thought that the upper and lower halves of the retina were unequally sensitive, because the lower half is subjected to more light than the upper half; except in the evening or when reading—when the upper half may be subjected to greater fatigue. Be this as it may, the difference between the readings obtained with and without the prism in position was surprising. It is considered essential that the effect of this difference in sensitivity of the two halves of the retina should be eliminated by taking the mean of an equal number of readings with and without an inverting prism in position. Tables IX, X, and XI give figures obtained for typical latices by this method. The use of the inverting prism reduces to a minimum the differences between readings obtained for a given latex by various observers, and it is proposed to improve the design of the apparatus by including an inverting prism in the eye-piece so that no difficulty may be experienced in bringing it into action.

Comparison of White Standards.—It was considered wise to take readings with the apparatus, employing a more universally accepted standard of whiteness than common salt. The most non-selective and perfectly reflecting surface is that produced by burning magnesium ribbon, and allowing the oxide to condense on a flat object. A layer of magnesium oxide was thus deposited on a block of iron to a thickness of approximately 0.5 mm. Table XI summarizes the results of determination of the color of a gray latex using Greatham salt and magnesium oxide, respectively, as the standard of whiteness. It was rather surprising to find that the readings were little lower with the magnesium oxide than with the salt. It had been anticipated that possibly the smoother texture of the magnesium oxide might make it easier to obtain a balance of the brightness of the latex and the standard; but this did not prove the case, as is indicated by the fact that the average deviation from the mean readings, and the maximum variation between readings, was slightly higher when using magnesium oxide than when using salt. Furthermore, presumably because of the high reflecting power of magnesium oxide for blue light, the latter, when used as standard, failed to indicate conclusively the obvious blue tint of a gray latex (see Table XI). A block of magnesium carbonate gave similar results, but it is doubtful whether these materials would be so readily cleaned as the surface of a block of salt which can be renewed by rubbing against another block. There are advantages in using a standard of whiteness which is less brilliant than magnesium oxide or carbonate, and therefore gives a higher reading for a particular latex.

Conclusions.—The results summarized in the present paper indicate that the apparatus described provides a simple and efficient means of determining quantitatively, and differentiating between, the color of commercial rubber latices. It is considered essential, in eliminating the effects of varying sensitivities of different eyes and different parts of the retina, to take the mean of at least ten readings obtained by the method outlined, with and without an inverting prism in the line of vision. It is suggested that latices be given a color index in the form of a fraction, the numerator of which shall be the mean reading in cm. at balance, employing a Kodak Wratten blue filter, series 48, and the denominator of which shall be the mean of a similar series of readings using a Kodak Wratten orange filter, series 22. This will clearly indicate at a glance whether the latex be yellow or blue in tint; the numerical value of the indices will indicate the brightness of the latex.

Latices of which the lower color index (whether blue or orange) falls between the limits mentioned below shall be designated:

40 or over	Excellent color
39 to 40	Good color
38 to 39	Fair color
37 to 38	Passable color
35 to 37	Poor color
Below 35	Very poor color

A latex giving a high color for orange but a low index for blue may look quite good, but in all probability it actually contains finely dispersed ferric hydroxide which will produce discoloration in dipped goods. It is however appreciated that latex giving a low color index may be perfectly suitable for certain applications; the fact that a latex has a low index of color should therefore not be taken as indicative of poor quality as regards rubber content.

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Note on the Deterioration of Raw Rubber by Manganese Contamination

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Introduction

The presence of excessive amounts of manganese has been found by Bruni and Pelizzola[1] to be associated frequently with tackiness in raw rubber. Bishop and Sekar[2] have described the development of unusual stickiness when rubber prepared from latex to which manganese salts had been added was subjected to a temperature of 50–55° C. for 300 hours. More recently Sackett[3] has found that the use of manganese salts in the manufacture of crude rubber gives a product which becomes tacky and weak on storage, and which, when vulcanized, has a lower tensile strength, a poorer resistance to aging and a poorer abrasion resistance than normal rubber. Bruni and Pelizzola when examining various samples of very tacky estate rubber found amounts of manganese of the order of 0.02 per cent, but were not able to form firm conclusions as to the manner in which such large amounts of manganese find their way into various grades of estate rubber. The present note describes an instance in which it has been possible to trace the cause of serious manganese tackiness in a large consignment of estate rubber.

Experimental

A large American consumer reported that a consignment of 150 cases of smoked sheet rubber from a Malayan estate had developed such very serious tackiness in the course of a storage period of two years that it had become virtually useless. It was stated that manganese had been detected in the rubber in amounts of the order of 0.01 to 0.02 per cent. Samples of the rubber were forwarded to the Institute for confirmatory test, and when examined were found in the worst cases to contain amounts of manganese of the order of 0.026 per cent, thereby confirming the findings of the American investigators. As the producer's name was known it was possible to attack the problem at its source and to attempt to discover the real cause of the high manganese content of the rubber.

When the estate was visited, it was found that no chemicals containing manganese were in use, nor had such ever been employed in the manufacture of the estate's rubber. There remained the one possibility that the estate water supply might contain manganese, but this possibility seemed somewhat remote because, of the many samples of Malayan estate factory waters that had been examined at the Institute over a period of years, none had been found to contain dangerous amounts of this element. The matter was however investigated. The estate had three separate sources of water, of which one was used only in emergency, during unusually dry weather. Water from this particular source had actually been in use in the factory about the time that the rubber under complaint had been prepared. Samples were drawn from all three sources. The water from the two more commonly used sources was found in both cases to be free from manganese, but it was

present in remarkably large amounts in the water from the emergency source. This water had a p_H value of 5.4, and was therefore distinctly acid. The content of total solids on the filtered water before and after ignition was 131 and 103 parts per 100,000, respectively. It is unusual for samples of Malayan waters to possess such a high total solid content, and this fact in itself would throw some suspicion on the quality of the water in question. Tests for manganese indicated its presence to the extent of 22 parts per 100,000, and it therefore seemed very probable that this water was the direct cause of the deterioration of the consignment of rubber under reference. It was necessary, however, to find reasonable evidence that the water and not the latex itself was responsible for the trouble. It was therefore considered desirable to prepare at the Institute an experimental batch of rubber from latex known to be above suspicion, using the manganese-contaminated water for rubber prepared from the same latex diluted with and soaked in a satisfactory water. Supplies of manganese-contaminated water were brought to the Institute, where two experimental batches of rubber were prepared from Institute latex, diluted to 1.5 lb. dry rubber per gallon with:

(1) manganese-contaminated water, and
(2) Institute water free from manganese.

The latex was coagulated in each case with 2.75 fluid ounces of 5 per cent acetic acid per gallon, and the rubber was machined into sheet on the following day between dry rolls. The wet sheets were then soaked in water for one hour before hanging to drain for two hours and before drying in hot air at 125° F. for 64 hours. Manganese-contaminated water was employed as the soaking medium for the rubber of batch (1), and Institute water free from manganese was used for batch (2).

When freshly prepared and also on arrival in London, neither of the two batches of rubber exhibited any trace of tackiness, and although the "manganese rubber" was slightly darker than the non-manganese or control rubber, it would have been classed by present day visual standards as first-grade rubber.

It was expected that the "manganese rubber" would show a greater tendency towards deterioration by oxidation than the control rubber and the following tests indicated this to be so.

(i) *Hardness (D 30) after Heating in Air for 18 Hours at 100° C.*—It is seen from the above test that, whereas the control sample hardened slightly in a normal manner under the influence of heat, the "manganese rubber" softened very markedly.

TABLE I

Sample	Hardness D 30 Mm. Initial	Hardness D 30 Mm. After 18 Hours at 100° C.
Control	1.47	1.66
"Manganese rubber"	1.43	0.87

(ii) *Ease of Mastication.*—The following figures indicate the number of grindings required to reduce each of the two rubbers to a fixed plasticity.

TABLE II

Sample	Mastication Number
Control	98
"Manganese rubber"	80

The greater ease of mastication in the case of the "manganese rubber" indicates a greater tendency towards oxidation.

(iii) *Oven-Aging of Vulcanized Material.*—The "manganese rubber" is seen to be weaker throughout than the control and to perish in a shorter time. The observations by Sackett[3] and those now presented are therefore in agreement.

TABLE III

"Manganese Rubber"				Control Rubber			
Time of Vulcanization at 148° C. Min.	Period of Aging at 70° C. Hours	Tensile Strength at Break Lb./Sq. In.	Elongation at Load of 1.04 Kg./Sq.Mm. Per Cent	Time of Vulcanization at 148° C. Min.	Period of Aging at 70° C. Hours	Tensile Strength at Break Lb./Sq. In.	Elongation at Load 1.04 Kg./Sq.Mm. Per Cent
117	0	1650	863	112	0	1740	865
...	48	1490	745	...	48	2050	766
...	72	620	...	...	72	1650	705
...	96	240	...	...	96	350	...
...	120	190	...	...	120	250	...

Discussion and Summary

A manganese-containing water supply has been found responsible for a serious complaint of manganese deterioration in a large consignment of raw rubber which had been stored for a period of two years. Manganese-contaminated rubber may possess initially, and retain for several weeks, the appearance of first-grade rubber, but experiments have indicated that, because of the greater ease with which it oxidizes, the danger of the development of softness and tackiness on long storage is greatly increased. It is important that on no estate should manganese salts be employed in the preparation of rubber. If complaints should be received as to tackiness in first-quality rubber, water samples should be despatched to the Institute for examination.

Acknowledgment

The rubber samples were examined by the staff of the London Advisory Committee, who provided all the results of the tests on the quality of the rubber.

Literature Cited

[1] Bruni and Peliszola, *India-Rubber J.*, **62**, 101 (1921).
[2] Bishop and Sekar, *J. Rubber Research Inst. Malaya*, **4**, 239 (1931).
[3] Sackett, *Rubber Age* (N. Y.), **35**, 232 (1934).

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Consumers' Crude Rubber Requirements

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A LIST of every requirement of the principal raw material of an industry as vast and as diversified in its interests as the rubber industry would be difficult to make. It is desirable, however, to consider the more important requirements for the rubber industry so that the producers may have a clearer conception of the consumers' needs. It is hoped that the result of focusing attention on the items discussed will eventually lead to the production of a type of rubber which may more nearly meet the consumers' ideal than any form produced previously.

Latex and its requirements will not be considered, for they are too specialized and should form a subject for separate discussion at another time. Nor will the present discussion consider ways and means which might be used by the producer to meet the requirements listed, for such considerations are beyond the scope of this paper.

Those requirements which seem to be general to the whole industry are as follows:

1. Uniform rate of cure of modulus to produce stocks of uniform strength and stiffness.
2. Uniform age resistance to guard against the sale and use of rubber which might be poor in this respect.
3. Cleanliness to improve the quality of stocks and eliminate the necessity of washing or straining to remove foreign matter.
4. Better packaging to facilitate handling and storage and prevent admission of dirt.
5. Freedom from diluents to avoid the presence of materials affecting compounding.
6. Freedom from deleterious materials to avoid premature deterioration of rubber goods.
7. Uniform plasticity to facilitate processing by avoiding dangers of scorching.
8. Low plasticity to eliminate part, if not all, of the expensive mastication process.

Other requirements are of considerable importance to some branches of the rubber industry, but they are not generally applicable and will not be considered in detail here. Thus, low water absorption is of importance to the wire insulation industry, and it has been and is being actively investigated. The development of a light-colored sheet has been studied for a number of years, but it is not of general interest, since it is confined to those requirements where color is important together with a lower plasticity. It is believed, however, that

practically all branches of the industry are interested in the properties listed.

Uniform Rate of Cure

One of the properties generally requested of rubber producers is that crude rubber should have a uniform rate of cure. However, unless some definite means are supplied to determine the rate of cure, it is useless to ask the producer to incorporate this property in his rubber. Rate of cure may be defined as the time and temperature required for a rubber when compounded in a standard formula to reach a degree of vulcanization characterized by certain well-defined properties. It is beyond the scope of this paper to discuss the various properties used for this purpose or to analyze the relative merits of the various proposed methods for determining the rate of cure.

However, it is pertinent to the present discussion to consider the adoption of a standard method of determining the state of cure desired, and to propose formulas for the purpose of testing rubber to ascertain its degree of uniformity. What follows is for the purpose of suggestion, with the idea that after discussion and consideration certain standard methods of test will be evolved so that the producing interests can study methods of improving the uniformity of their material.

Best Property for Measuring Cure. Articles made of soft vulcanized rubber (as distinguished from ebonite or hard rubber and also from uncured rubber) are manufactured for the purpose of fitting the intrinsic properties of the rubber hydrocarbon to the needs of the article and for the service under consideration. The time and temperature of vulcanization are largely controlled by the economics of the factory and the compounding is designed to give the product optimum quality, with due regard to quality after aging either in service or in storage.

With this in mind, compounders usually balance their curing agents so that the stock will have a definite state of cure, dependent on the article and its service requirements. Unless these requirements demand a positive under- or overcure, the stock is usually compounded so that it has a technical "best cure" at the time and temperature required by the manufacturing process. One way of fixing the state of best cure is by a hand test which reflects both modulus and tear resistance.

Since we are primarily concerned with the practical use of rubber, we should use a similar method for determining the state of cure of a stock used for rubber testing. This stock should be a pure gum type, for loading masks the effect of the rubber variations, and it should recognize the universal use of organic accelerators. The accelerator used should be quite generally accepted as a standard, should be widely available in a constant degree of purity, and should typify, if

possible, a class of accelerators. As a basic type accelerator, diphenylguanidine suggests itself. The following formula and cures are suggested:

Rubber	100.00	Sulfur	4.00
Zinc oxide	5.00	Diphenylguanidine	0.75

Cure: 20, 30, 40, 50, 60, 80 minutes at 274° F. (134° C.).

This stock will give a "best cure" in about 50 minutes.

An accelerator of the acidic type is also desirable for examining rubber. Mercaptobenzothiazole is suggested, and the following formula is believed acceptable:

Rubber	100.00	Sulfur	3.50
Zinc oxide	6.00	Mercaptobenzothiazole	0.50
Stearic acid	1.00		

Cure: 20, 30, 40, 50, 60, 80 minutes at 260° F. (127° C.).

This stock gives a best cure in about 50 minutes.

A large number of rubber samples have been examined by these formulas, and the conclusion has been reached that plantation smoked sheets do not seriously vary in rate of cure, if we agree with what has been said above that the rate of cure is considered to be the time required to vulcanize the compound to a technical best cure as judged by hand tear test in a specified formula at a given temperature.

VARIATION IN RUBBER. This statement is not intended to imply that rubber does not vary however, for, as tested in the mercaptobenzothiazole formula, at the best cure there will be marked differences in the modulus of various samples.

Modulus is an important property and should be uniform, if possible, for it is used widely in practice. It serves as an index of quality of a given sample of stock. As outlined above, a stock is designed for certain purposes, and the details of manufacture are worked out. In order to control the stock in production it is necessary to apply some unit of measurement of its important properties. The modulus is generally used for this purpose.

For control purposes raw materials are subjected to test before they enter production. Experience shows whether all materials must be put through a compounding test using standard components of the batch, or whether simpler chemical or physical tests suffice. Rubber, however, can be tested only in a compounded and cured stock. It is logical, therefore, to apply the same unit of measurement of quality in this test that is used when testing the finished batch. Modulus is the unit usually adopted, because other tests are more expensive and take too much time to serve for control purposes.

The mercaptobenzothiazole formula given is useful for this purpose. If rubber is compounded in this formula, rapid results can be obtained, and the rubber can be graded according to modulus. Furthermore, experience has shown that on the basis of the test obtained, the rubber can be blended to give the modulus desired. Thus we can be assured that the physical properties of the finished batch will not vary because of the rubber.

In order to avoid a misunderstanding between what has been said about modulus and what was said about cure or rate of cure, it should be pointed out that, if a rubber gives a high modulus test in the time selected (which should be such as to give approximately a best cure), a decrease in time of cure will bring the modulus down. But it also alters the state of cure which seriously affects the performance and, therefore, the quality of the finished stock. It is better to bring the modulus down by blending such rubber with rubber which shows a low modulus. Low-modulus rubber should be treated in a similar manner.

In working out such a scheme of blending, it is necessary first to run a number of samples of rubber and plot a distribution cure. The range of modulus found to be average can then be selected. Rubber from this average range is then used in developing any stock, and in production the rubbers can be balanced in proportion to modulus.

The modulus property is important in lightly loaded stocks. Loading masks modulus changes, and variations in the modulus of the rubber are not so clearly reflected in highly loaded stocks. Whether it will ever be possible for the plantations to produce a rubber of uniform modulus is open to question. The difficulties to be overcome are very great, but the elimination of blending and the improved properties of the final products make it desirable to produce a crude rubber with a minimum of variation in this respect.

Uniform Age Resistance

The manufacture of rubber from the latex from seedling trees did not allow the properties of the rubber from any single tree to affect a large amount of finished product. With the development of large areas of clonal plantings, it becomes advisable that an intensive study be made to assure the consumer that clonal rubber of various types possesses no undesirable properties. The clonal rubber from different geographical locations and the effect of different soils in the same general location should be studied.

The formulas given for testing the rate of cure are suitable for studying age resistance. The diphenylguanidine stock might be aged for 12 days in the Geer oven at 70°.

The mercaptobenzothiazole stock may be aged in the Geer oven for 12 days at 70°, or it may be aged in the air bomb or the oxygen bomb. Increase in modulus should be observed, or, if oxidation has proceeded farther, the decrease in tensile strength should be used as an indication of age resistance.

It may be desirable to see whether a natural deficiency of antioxidant could be corrected for by the addition of organic antioxidants. In such a case, one per cent of phenyl-β-naphthylamine should be added. The formula then becomes:

Rubber	100.00	Stearic acid	1.00
Zinc oxide	6.00	Mercaptobenzothiazole	0.50
Sulfur	3.50	Phenyl-β-naphthylamine	1.00

It will be necessary to collect a great deal of data to establish the relative age resistance of various clonal rubbers. Conclusions cannot be drawn fairly from a few tests. The rubber should be collected from a large number of trees in different places and manufactured in a strictly comparable and practical manner. The curing agents should be so adjusted that the samples cure to the same state in approximately the same time.

For use as a standard sample, some clone should be selected which gives properties comparable to those of the usual seedling rubber. Provision might be made to ship this clonal rubber directly from a given place to the research station carrying on the work.

Cleanliness

The relatively high consumption of amber crepes and similar grades of rubber is evidence that absolute cleanliness is not absolutely essential for compounding all rubber goods. There are a number of rubber articles, such as inner tubes, hot water bottles, and the like, which do require rubber of the highest possible degree of freedom from foreign matter. There is no advantage other than the economic one in using rubber with a small amount of dirt in it. In a tire tread a small amount of sand and bark has no doubt been tolerated; however, there is little question but that a clean rubber would be better. A small particle of sand in an inner tube will soon cut through and develop into a leak, so that freedom from dirt is a prime requisite for this type of stock.

The crude methods used by the native plantation owners preclude the possibility of ever getting more than a small amount of clean rubber from that source. The European plantation, therefore, is and probably always will be the chief supply. The quality of rubber from these plantations, however, should improve continuously if these plantations want to hold their leadership in this field. Rubber manufacturers have always had to find ways to clean and use a more or less dirty material for special purposes. In the earlier days it was necessary to use large quantities of wild rubber, and the wide fluctuations in price which have occurred have made it necessary for economic reasons to adapt the poorer grades of rubber to products which would never have called for such raw material had a constant supply of clean rubber been available.

There is no method of measuring quantitatively the cleanliness of rubber. Dependence must be placed on a visual examination, and it is difficult to see all the finer particles of sand. The performance of some cured stocks in practical use will show the effects of sand and bark. Great care in handling latex, followed by clean smoking and good packing, will go a long way toward the realization of a superior rubber. The necessary precautions to produce a really clean rubber

may cost a small amount of money, and this added expense might be hard to collect as a premium, but the establishment and maintenance of a position of superiority over the poorer grades and the ready market for this rubber should justify such slight expense. It is possible and, if the example of other industries is followed, it is probable, that the clean rubber may be produced at no higher cost than the present material. The requirements of the consumer for a really clean rubber are great and worthy of serious consideration by the producers.

Better Packaging

Clean rubber demands a suitable container; otherwise, the money spent in removing the dirt on the plantation is wasted. The veneer chest, which is the standard container, has the disadvantage of splintering when broken and of giving off splinters to the sheet during storage. There has been evidence at times that veneer chests of inferior quality have been used. These chests break easily in handling and form a large amount of small splinters which adhere to the rubber.

Jute wrappings have been used for years, but rubber packed in them is not tenderable. They have been adopted for reasons of economy by consumers who purchase in eastern markets. The rubber is examined before packing and no further examination is required. Rubber packed in this manner is not as easily stored, and the bales are apt to become badly distorted during transit to the destination.

If rubber were always handled directly to the consumer with only a short period of storage, the problem would be fairly simple. Rubber is a commodity which can be stored, and is stored, for relatively long periods of time. That rubber, then, which is sold on the open market must be packed in a case that will contain as much as the present case and will not splinter. It should be light in weight to keep down freight charges and should withstand rough handling. It should be cheap. There is a real demand for such a container.

Freedom from Diluents

There is no complaint about the market grades of plantation rubber with respect to the presence of excessive amounts of nonrubber material. There have appeared recently, however, some samples of new forms of rubber which contained large amounts of added substance designed to prevent adhesion of the rubber particles and so preserve the original form of the rubber.

Consumers of crude rubber are glad to welcome new forms of their principal raw material and to adapt it to their requirements if there is any advantage in experimenting with it. Large percentages of starch, dextrin, zinc stearate, talc, or other material is, however, a positive deterrent to the use

of such new products. There may be a few places where the nonrubber materials in large proportion would not be objectionable, but the annual consumption of crude rubber for these purposes is extremely small.

Any form of rubber which retains more of the natural nonrubbers from the original latex is sure to meet with considerable opposition. These substances affect the rate of cure and certain properties of the finished article. If compensation can be effected, special handling is required which is not always economically feasible.

Rubber prices are always based on the current market price of an accepted standard type of crude material. This is, and probably will be for some time, smoked sheets. Naturally, therefore, any form which contains more nonrubber than smoked sheet will be considered on the basis of its rubber content. Those claims of higher yields and greater returns obtainable from methods of manufacturing crude rubber which are based only on the inclusion of amounts of nonrubbers greater than those occurring in standard types will usually be found false. The same applies to those claims for types which call for added nonrubber materials.

The consumer will probably always demand that crude rubber contain the minimum amount of nonrubber material compatible with high quality of both crude rubber and finished articles.

Freedom from Deleterious Materials

That rubber should be free from the presence of any material which would adversely affect the service obtainable from a rubber product is self-evident. Fortunately there has been little difficulty with plantation rubber from this cause.

New methods of treating coagulum are proposed from time to time by people who are interested only in the sale of a proprietary material and not in the future of the resultant product. In order to insure against the danger of producing an inferior rubber, the plantations should make sure that any deviation which they propose to make from the standard accepted methods has been approved by the technical organizations established for their benefit.

There has been some trouble due to a faulty water supply on a plantation. The water supply systems of all plantations should be checked and, if found faulty, correctives should be applied immediately.

Crude rubber should always be prepared according to an accepted standard method from materials of known satisfactory composition.

Uniform Plasticity

Crude rubber from different plantations, and even from the same plantation, shows considerable variation in plasticity. The studies made so far have not resulted in any improvement of uniformity of this property. Processing varia-

tions result from variations in the plasticity; in order to avoid these variations, constant control of the amount of plasticizing is necessary.

The use of accelerators which are sensitive at low temperatures has accentuated the difficulties caused by the rubber. Crude rubber consumers are restricted in their study of this problem by their geographical distance from the point of production. It is a matter for the producer, working with technical and research organizations, to investigate fully.

The role of oxygen in softening rubber is well recognized. Studies of drying temperatures and the content of natural antioxidants in the latex might throw some light on this matter.

Low Plasticity

A remarkable change would be effected in the whole rubber manufacturing industry if producers were to find a method of making a rubber which was soft enough to use directly. Such a rubber would be worth a great deal but the low plasticity must be obtained at small cost because cheap power and efficient machinery keep the consumers' costs of plasticizing down to a low figure.

Some types of manufacture which require soft rubber could afford to pay more for a low-plasticity material, and the development of a soft rubber, with properties equal to those of present crude rubber, would be welcome.

Soft rubber, however, would require a special type of package. Examination would be impossible and long periods of storage would not be favorable. Such a material, therefore, would require more direct contact between producer and consumer.

Conclusions

In this brief summary of requirements, much has been left unsaid. It is difficult to be specific, for the requirements of the rubber manufacturing industry vary widely. It is hoped, however, that this presentation will focus some attention on the subject, and that eventually a more definite idea of the requirements of the various consumers will be presented so that plans of research in rubber-producing parts of the world can be made to develop the products needed by the consumer. This would also aid in the development of closer contact by both producer and consumer, which is desirable in any industry.

The formulas suggested are open to criticism and it is hoped that if those suggested are not adopted as standard, others more generally accepted will be evolved so that there may be a universal agreement on the method of testing certain properties of rubber.

It may be argued that a rubber which combined all the properties mentioned would be ideal, but it is well to set up an ideal to strive for, so that through the collaboration of producer and consumer, it may perhaps be realized.

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Rubber Production

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SACKETT'S paper seems to have crystallized the whole situation. However, it is one thing for Sackett to say what is wanted and quite another to get it accomplished at once in Malaya.

First, the position of the Rubber Research Institute in the "hodgepodge" of organizations which make up the industry and its powers should be clarified. The institute is not a government institution in the accepted sense of the word, nor is it a business organization. This means that it has no power to force the planting community to adopt any particular method of manufacture and no power to change the methods of marketing now in vogue. The influence of the institute does not extend beyond the spheres of advice and suggestion.

On the one hand, the institute has the planting community which aims solely at satisfying a broker's standard; on the other hand are the rubber chemists who want a rubber with qualities not taken into account by the broker and who perhaps sometimes feel that the broker has not always, even by his own standards, given rubber of the grade paid for. The institute is in a difficult position but is doing all it can to persuade the planting community to produce an article which will conform to brokers' standards and at the same time possess in greater and greater degree, as time goes on, the other qualities which the chemists require. This has been the institute's policy, and by persuasion something is being achieved which should eventually be of value to all. Sackett wants:

1. Uniform rubber in three directions:
   a. Rate of cure.
   b. Plasticity where the plasticity corresponds to a fairly soft rubber.
   c. Aging properties.
2. Rubber with lower water absorption.
3. Clean rubber.
4. Rubber free from dangerous and deleterious materials.
5. Light colored sheet.
6. Better packing.

He points out that, in self-defense against the prevalence of some of these defects, users have developed means of overcoming them; he indicates almost after the manner of the canny Scotch planter himself that, while the user wants a general improvement in all these qualities and would welcome

a better article, he would probably not want to pay a premium to obtain it in view of the various means which he has developed for utilizing poor rubber. The institute, then, should do all in its power to give the user a rubber which will require neither this extra processing nor a higher price.

Uniform Rate of Cure

In order to outline the prospects of achieving uniform rate of cure let us examine the difficulties and see what has been done recently toward achieving it. The variation in sheet rubber is due briefly to (1) source of latex, (2) methods of tapping, (3) changes between tree and factory, and (4) lack of finesse in factory procedure.

Source of Latex

Latex is not and can never be a synthetic laboratory chemical of constant composition. It is a biological fluid and not a special chemical. It comes from a tree which is dependent for its very existence on sun, rain, and soil. Because the tree is a tree, it is subject to natural physiological cycles of wintering, refoliating, flowering, and seeding. Rubber trees differ slightly in genetic strain. They grow differently on different soils, and it is ridiculous for us to expect to obtain latex of constant chemical composition all the year round. The factors which affect variation in latex are (1) season of the year, (2) age of the trees, (3) geographical situation, (4) state of the soil, and (5) genetic strain; these variations are of the sort which cannot be prevented by any known means. Variation due to these causes is inherent in the trees and their locality. Variations occur not only in the rubber content of the latex but also in the content of nonrubber constituents and nitrogenous and mineral materials. The chief variations occur with the seasons. For instance, in Malaya, in February and March when trees are wintering, the dry rubber content is high; in April and May when trees are refoliating the dry rubber content is at a minimum; when refoliation is completed, the dry rubber content gradually rises until it reaches a maximum in July and August; in the wet months of September and December the dry rubber content falls again. Also the ash of the latex is low during the wintering period and again when the seeds are falling, which occurs in July and August.

These inherent variations result in variable rates of cure and are the fundamental obstacles standing in the way of achieving uniformity.

Methods of Tapping

The method of tapping superimposes another variable. The fact of repeatedly opening a tree and causing it to emit

latex imposes a strain, and the greater that strain, the greater is the variation in the composition of the latex. The greater the frequency of tapping or the longer the cut, the greater is the variation in composition. In Malaya and the Netherlands Indies the tapping systems most commonly used differ in severity and tend towards different degrees of variation.

The daily alternate-monthly system of the Netherlands Indies involves tapping the trees each day for a month and then resting them for a month. This results in a constant change in latex composition over the whole tapping period. There may be a steady fall in dry rubber content from 44 to about 27 per cent during the month, and the crop of each day is different.

The alternate-daily continuous and the ABC systems of Malaya involve continuous tapping every alternate day for a year or more. The result is that after the first few days the latex reaches a sort of equilibrium in composition, apart from seasonal and other inherent variations. The variation in composition is smaller than in the Sumatran system and this should, in theory, make for greater uniformity in the rubber. If all estates in all producing countries found it economic to tap on some such continuous system, this might smooth out some variation. Problems concerning estate management and tapping costs will undoubtedly prevent the adoption of a uniform system, and we must therefore conclude that the raw material (latex) will always be variable. The variation will be partly inherent and partly due to tapping methods.

Changes between Tree and Factory

Whenever latex is won from a tree under practical conditions, it is contaminated with bacteria. This contamination cannot be prevented in practice. Cultures on dextrose agar show at 10 A. M., six million bacteria; at 11:30 A. M., sixty million; and at 1:30 P. M., two hundred million.

The acidity which the bacteria produce causes premature coagulation in the field, which can be prevented by the addition of small quantities of either sodium sulfite or ammonia. But the amounts in which they are used are not sufficient to kill the bacteria. They do not sterilize the latex, and, although the latex may appear to be satisfactory, the bacteria are still at work producing decomposition in the latex constituents. Varying degrees of bacterial contamination and activity from day to day can, therefore, make only for a further adventitious variability in latex composition. For this variation the obvious remedy is speed of collection, but the speed maximum is variable according to the lay of the land, state of the roads, and distance from the factory. In practice we cannot avoid harvesting an inherently variable material and one charged with bacteria which must contribute a further adventitious variable. This means

that, if we are to produce uniform rubber, the factory must do something to smooth out these variations without introducing any new ones.

Developments in Factory Procedure

Old-Time Factories. Ten years ago transport of latex was, on the majority of estates, by man power. All collectors carried their latex to the factory. Those on outlying sections came in late. The larger estates often had a number of small factories because there was too much loss of rubber through clotting if all coolies had to walk to one place. The factory usually contained wooden or tiled tanks for coagulation. These were 9 to 11 inches deep. The machinery for sheet manufacture consisted usually of two pairs of light, smooth-steel, even-speed rolls and a similar pair of grooved rolls for marking the sheet and imprinting the estate name. The machines were side by side and usually remote from the coagulating tanks. The latex was sieved through coarse sieves straight into the coagulating tanks, diluted with water, and treated with acid. Now, it rains in the tropics, and when cuts were low sand and dirt were splashed into the cups. Sand particles are frequently as small as 1/200 inch, and the sieves used were about 40 mesh. Sand does not settle out of raw latex easily. A viscosity of 14 to 20 centipoises prevents its settling. When latex is diluted with an equal volume of water, the sand settles easily. Thus, the sand went into the coagulating tanks. Dilution and coagulation brought it through into the rubber, because the subsequent simple rolling out into a sheet only embeds the dirt more firmly. The dilution of the latex left a good deal to be desired in many cases because quite often no hydrometer or metrolac was used to assist in arriving at a fixed standard of dilution. The amount of acid added for coagulation was usually more than was necessary, because, with machines and tanks remote from each other, it was necessary to carry each piece of the wet junket or coagulum by hand from tank to machine. This meant that the coagulum had to be made tough enough to be carried; in other words, it meant excess acid Even then the tough coagulum was deformed by being carried about. It was mutilated still more either by being walked on to press it thin enough to enter the first machine, or else by being crudely rolled by hand with a wooden roller on a flat table. By the time the pieces were ready to enter the machines, they were by no means uniform in thickness and the irregularities persisted through the machining process. In the machining process itself the coagulum was elastic rather than plastic, it did not roll out easily, and the finished sheet was always too thick. Little or no importance was attached to the average thickness of the sheets or to the prevalence of very thick places at the ends or sides. The sheets might or might not be soaked for a while in water after machining. They might be

hung in a blazing sun to drain for a long or short period or they might be piled in stacks with no draining period at all and left sometimes overnight before being taken into the drying chamber. The smoke houses or drying chambers were numerous and large. Some were simply large barns with a fire in a pit in the floor; others had a brickwork furnace on the floor which might be fed from outside or inside the building itself. Temperature control was practically nil. Humidity might be anything. Drying thick irregular sheets was a prolonged and an irregular business which might take 8 to 14 days, and even then many white or virgin patches might be observed on sheets which were removed for packing. These wet patches had to be cut away by the sorters. Some sheets which by chance were less thick than others might be brought out several days before more irregular ones from the same crop. These were naturally lighter in color. Similarly, by some accident in design or location, one building might normally dry sheets more rapidly than its neighbor. This gave rise to much variation in color. The sorting, grading, and packing were usually carried out in a badly lighted building by operatives who sat on the floor, held up each sheet to such light as there was, and cut out those offending patches which they happened to spot. Naturally, many were overlooked.

Of course, there was room for much improvement. Quick transport and centralization of manufacture might overcome the waste of man power on two or three complete small factories on one estate. The fact of small factories in different parts of one estate makes for variation, and greater uniformity should result if all the latex from the whole estate could be bulked before manufacture began. This should smooth out variations due to age of trees in different sections, the situation of the blocks whether on good or bad, hilly or flat land, and the adventitious bacterial contamination. Dirt and sand should be prevented from appearing in the sheets. The wooden and tiled coagulating tanks must harbor bacteria by the million in crevices, making a bad job worse. Tanks and machines should be better arranged and this mutilation of coagulum by carrying, foot-stamping, and hand-rolling should be abolished. The coagulum should be soft and plastic, because if one is to smooth out variations at all, one must aim at a very thin sheet so that the rubber from one day's crop will not differ from that of another day by the presence of large amounts of occluded serum substances of doubtful composition and varying effects on properties A thick sheet left about at a low temperature must have behaved not unlike a slab, and bacterial decomposition must have produced the natural accelerators in it, thus affecting its rate of cure. This process must have continued in many cases in the slow drying which took place in the smokehouses. Thus thin sheets, washed and drained and quickly dried, are indicated. Drying should be better controlled.

Modern Developments. The institute's officers have

been able to exert a useful influence during the last four or five years, in so far as Malaya is concerned. About the time a great deal of machinery was becoming ready for replacement the slump in rubber prices compelled estates to consider such things as man power and other factory costs. Estates and engineering concerns were only too pleased to consider the institute's suggestions for new machinery and better factory arrangements generally. About this time also there was a severe epidemic of smokehouse fires, and many estates were free to build new smokehouses at the expense of the insurance companies. The institute had taken records of the output of a large number of estate sheeting outfits and had found that few of them produced more than 300 pounds of rubber per hour. The coagulating tanks and therefore the pieces of rubber were too narrow and consequently too light. The rolls themselves were too slow, and no attempt was made to synchronize speeds to allow for the increased length of a given piece of rubber after each passage through the rolls. Further, each operative consumed as much time in picking up material from one side and finally passing it sideways to his Tamil neighbor on the other side as he did in actually putting the rubber through the rolls. This was an inefficient business, and here was the institute's chance to persuade estates to produce better quality rubber under the guise of being more efficient and cheaper. Success followed. At the same time authorities in the Netherlands Indies were doing likewise. At the suggestion of the institute, engineering firms designed batteries of machines set in column instead of side by side, with water-filled trays between each machine. Wider rolls were standardized so as to make possible the use of deeper coagulating tanks lined with aluminum. The rolls were synchronized for speed so that pieces of coagulum followed each other end on end through the whole battery of machines with no delay and no strain on the operative. Instead of three machines, there were five or six so that a thinner sheet could be rolled without recourse to foot-stamping and hand-rolling. The output of a battery was actually raised in this way from 300 to 2000 pounds of rubber per hour. These new sheeting batteries lend themselves to proper conveyance of the coagulum because it is possible to float or slide the coagulum to the first machine, after which it passes in a dead straight line through the whole outfit. The first new layouts had line-ahead batteries and a central sloping water chute down which the pieces of coagulum were shot from the coagulating tanks set on either side of it. The operatives merely lifted the pieces and shot them down to the machines. Still more recently the chute was replaced by a central water trough so arranged that, by flooding the coagulating tanks, the coagulum could be floated all the way from tank to machine with no lifting or carrying at all. The rapid production of thin uniform sheets which could be dried quickly and evenly with very few thick virgin patches thus became possible.

The advent of high-output machinery and the better factory layout which it made possible, resulted in the centralization of manufacture on many estates which previously had two or three subsidiary factories. Reorganized factories included in their outfits at the institute's suggestion large bulking tanks. These have sloping bottoms and serve the dual purpose of bulking and sand removal. Here the latex is diluted to a fixed dry rubber content and allowed to deposit sand. The clean latex is run off through fine sieves into the coagulating tanks from a high-level cock leaving a residuum of sand-contaminated latex.

Thus in a number of factories low operating costs were combined with (1) the removal of some sand, (2) the ability to prepare, convey, and handle a very soft coagulum from which serum is readily squeezed out, and (3) an adequate number of rolls to give thin uniform sheets.

The institute's next step has been to encourage the erection of small-compartment smokehouses with accommodation for one day's crop in each of four compartments and no reserve space. This was a dastardly attempt on the institute's part to make sure that an efficient factory plant should be worked efficiently, because with no reserve drying space the smokehouse is the key point in the whole outfit; if the latex is not correctly coagulated and the coagulum not correctly handled and machined thin, the rubber is not dry in time and the whole estate is thrown out of gear. The factory must be operated efficiently. A number of estate managers have either fallen into the trap or gone into it with their eyes open. The result has invariably been the same—efficiency. The wet-machined sheets are hung on trolleys to drain for 3 hours and then trolleyed straight into their compartment for drying and smoking. Temperature and ventilation control are both far easier in these small buildings, and drying is uniform and efficient. The final result is uniform, clean, and reasonably quick-smoking, following uniform latex handling and manufacture.

Sorting and grading have been improved and cheapened by the adoption of large discs of ground glass illuminated from below. Quite small blemishes are easily spotted and removed.

Thus the last few years have seen some progress in the right direction. More and more estates are reëquipping. The institute could never have persuaded estates to reëquip for the avowed purpose of improving the inherent properties of the rubber but only for the reason that reëquipping also gives greater efficiency and reduces costs.

Drying Period. Why is the institute aiming at a drying period of four days and not two days or one day? The answer is that in this matter it is advisable to make haste slowly. The sheet should be dried without undue bacterial maturation and the variability in cure which it may produce, but other defects may be introduced by drying too quickly. In

preliminary bomb-aging work with simple rubber-sulfur mixings from sheets dried in various periods, rapidly dried sheets have always given poor results. Similarly, manufacturers have complained that the light-colored, quickly dried sheet is too tough while the darker sheet is softer and easier to handle on the rolls. So far not enough evidence is available on drying and its direct effects on inner properties. This may prove to be important. Hence the institute believes that the four-day drying period at present is the shortest safe period.

Factory Centralization. To what extent can bulking be carried out from very large areas in one mighty factory prior to manufacture in order to achieve greater uniformity? The safe high limit of bulking—in other words, of centralization—is not high in practice. No matter how good transport facilities are, it takes a long time to move several thousand gallons of latex from the fields into the bulkers; premature coagulation and other troubles would undoubtedly prove troublesome, and day-to-day variation introduced adventitiously from these troubles might well be as great as the variations which the bulking set out to remove. For easy handling, the practicable bulking limit seems to lie in the zone of 500 to 700 gallons, and it is unwise to exceed it. Practical difficulties upset theoretical considerations badly here. In this connection Sackett himself has provided us with some illuminating results which point unmistakably to the conclusion that the theory of large-scale bulking is one thing and its practice and practical value, quite another. Nevertheless, the growing movement towards better and more uniform preparation of rubber is in the right direction. It will eventually result in an estate product of better all-round quality. A perfectly uniform product from all Malaya all the time cannot be expected. Seasonal variations in rate of cure alone will prevent it because even with better factory procedure these variations are not eliminated. Even with a uniform alternate-day tapping system, the bulking of rubber from a month's crop still shows seasonal variations as between one month's crop and another, so that an all-Malayan estate rubber of uniform cure is an ideal state which will probably not be achieved for a long time.

Uniform Plasticity and Aging Properties. Evidence is lacking on these points. The institute expects its work directed towards finding ideal drying and smoking conditions to lead to the goal of greater uniformity in these properties. That is for the future.

Uniform Water Absorption. Experiments are in progress on the effect of various preparation factors on this property of rubber, and it will be easily possible to smooth out much of the present variation by taking greater care at certain essential stages. Without very special pretreatment of latex, however, it will not be possible to reduce the average water absorption to a value much below 0.4 per cent. Chemists who hope for a rubber with water absorption of the order of 0.001

per cent or less, will never get it in rubber manufactured even by present methods for present market requirements. The institute is working on special methods of preparing low-absorption rubber, but progress cannot be reported at this stage.

Dangerous Chemicals. With regard to the use of dangerous chemicals on estates, there is no cause for worry. One or two estates did use sulfuric acid for a while but the institute's warning against it has been effective. It is not certain that sulfuric acid is really dangerous when properly used as it was in these cases. No estates are using manganese- or copper-bearing chemicals. There was a recent case of manganese contamination which affected Sackett and, later on, the writer. Here the source of manganese was traced to an exceptional water supply. There was no question of the estate's having deliberately used a dangerous chemical. Nobody knew at the time that the water employed was other than quite satisfactory. That sort of defect will not appear again in rubber from that source and quite probably not anywhere else. Sackett suggests that all estate water supplies should be checked for the presence of manganese. A large number have already been checked, and this necessary work will continue.

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On the whole then, in so far as estate smoked sheet rubber is concerned, Malaya is turning out an increasing amount of rubber which is more carefully prepared than it was a few years ago and which should prove more acceptable to users generally on Sackett's criteria. If users were able to contact directly with selected estates, the benefit of the improved manufacture should be felt at once; but in the absence of direct contact and assuming that brokers' consignments are usually mixed, with the result that each may contain rubber partly from reorganized estates and partly from estates which for some reason have not reorganized, users may not feel the effect of the present movement for some time.

The production of estate crepe has not changed appreciably in recent years except that fewer estates are making it.

The manner of production of native sheet from larger holdings in Malaya is improving, and on many of them the product is quite as good as the average estate product of ten years ago. These rubbers are not to be expected to be quite clean and free from sand and dirt. That will come in a few years.

The rubber from very small holdings is no better prepared than it was six years ago. It contains, as it always did, dead spiders, leaves, sand, dirt, and betel nut juice, and is manufactured in haphazard fashion. Most of it is bought in the form of Singapore blanket which finds a ready sale in the United States. The institute's small-holders' advisory service is trying to improve the rough and ready technic of

these small producers by persuading them to clean their latex more thoroughly and by taking greater care in coagulation. They are being encouraged to dry and smoke their own rubber properly. In spite of these efforts, not much improvement in native sheets or in Singapore blanket can be expected for some time to come. It is one thing to show a Malay holder what to do and another thing to get him to do it when you are not there.

A great deal of the rubber of which Singapore blanket is composed comes over for manufacture from the Netherlands Indies which is outside the institute's sphere of activity and influence; most of it is far worse than the Malayan counterpart, at least in appearance. All is grist that comes to the Singapore mills, and, even when the cleanliness of rubber has been improved in Malaya, its admixture with worse rubber from over the water may discount the institute's efforts to some extent.

Special Rubbers

If users required extremely soft rubber or rubber of extremely low water absorption, direct contact between user and producer would be an absolute necessity. In so far as rubber of low water absorption is concerned, it has already been indicated that, if we are to make a sheet which will pass in the present markets, no modification in technic will reduce its water absorption to a low enough value. If by special methods we do reach the correct value, the rubber itself will not then have an appearance which would make it acceptable as a market grade. Such rubber would need therefore to be made directly for the user. A similar state of affairs would arise in the case of extremely soft rubber. A user who wanted an extremely soft rubber and who paid a premium for it, would probably also want the producer to guarantee a fixed plasticity-tolerance limit. Estates in Malaya could not do this at present owing to the absence of executives with technical training.

Air-Dried Sheet. Sackett indicates a possible outlet for sheet rubber dried in hot air. Such material is being produced in Malaya, and fair amounts could be made available to users on demand. If rubber-sulfur bomb aging tests are any criterion, however, they would indicate the possibility of slightly poorer aging properties in hot-air-dried as against smoked sheet. In the institute's experiments with smoked and air-dried sheet from the same latex, such results have been obtained regularly.

Rubber Powders

Rubber powders are not yet in commercial production in Malaya although a plant is at work in Ceylon. Their cost of production must certainly be greater than that of sheet,

and a premium in price will be necessary if their production is to be worth while in the East. Dusting will, as Sackett suggests, need to be carefully controlled and reduced in amount to the minimum compatible with safe transit. Further, the user should be prepared to find variations in properties just as they are found in latex and sheet rubber.

Vulcanization and Testing of Rubber

Sackett makes a number of useful suggestions for methods of testing. In Malaya so far only simple 100–10 rubber-sulfur mixes have been tested. The technical officers of the institute's London Advisory Committee carry out tests in accelerator mixes. The policy has been for the London colleagues to test in all types of mixes those samples which have seemed abnormal. The writer cannot say off-hand, however, whether or not the mixes employed in London are identical with those now suggested. It would be an excellent thing if American chemists, the Rubber Research Institute, its London Advisory Committee, and probably the English manufacturers could adopt standard mixes and standard testing technic. The sooner unanimity is reached, the better. The institute and its London colleagues will be only too pleased to discuss proposals for unification of testing. At the same time it might be possible to agree on some standard methods of deciding the presence or absence of mold and sand.

Conclusion

The institute welcomes contact with users in America. There have been a few occasions when users have approached the institute direct on matters in which it could be of obvious assistance. A notable recent case was that of the manganese deterioration brought by Sackett's organization. In this case the institute was able to be of some assistance and was itself benefited. Such coöperation is excellent, and will be very welcome in Malaya.

It would be well also to establish some single committee or organization as a channel through which samples, reports, complaints and suggestions could be circulated freely to American users from Malaya and the London organization, and received in both places from America. If there were a constant contact, for example, between a technical subcommittee of the AMERICAN CHEMICAL SOCIETY'S Rubber Division, the technical subcommittee of the London Advisory Committee, and the Board of the Rubber Research Institute, users' requirements would always be known, views could be exchanged, suggestions could be made, word battles fought, and samples and batches of new materials passed forward from Malaya and London for American works test.

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Comments

THE practice in rubber factories is to control carefully by specifications the quality of carbon black, zinc oxide, oils, etc., that are used in various compounds. Shipments that do not meet specifications are rejected because they have some undesirable effect on the rate of cure, modulus, tensile, hardness, etc.

When it comes to the purchase and approval of crude rubber, however, our attitude is most inconsistent. The practice is to buy crude rubber by grade according to color and cleanliness. No attention is paid to the variation in rate of cure, in modulus, in effect on processing, etc., of the one material which is used in greater volume than all of the others combined.

Differences of several hundred per cent in modulus at 700 per cent elongation have been shown in a standard mercaptobenzothiazole test recipe using No. 1 ribbed smoked sheets from English estates. By using selected rubbers that show a very slow cure on the one hand and extremely fast cure on the other, in third-section tires with the standard curing rubber, undercure, optimum, and overcure sections have been obtained in the same tire.

The rubber technologist has been forced to develop accelerators, age resistors, and eveners, and to resort to selection and blending of rubber in order to produce a uniform product. All this has meant added cost, and in all probability quality is not all that it would be if a uniform-curing rubber could be obtained in the first place.

In addition, the rubber technologist must struggle with extreme variations in workability or plasticity of the rubber as well as variable amounts of foreign material.

It is entirely possible that the producers of crude rubber do not quite appreciate the difficulties encountered in the consumers' factories. On the other hand, the consumer may be expecting more than it is possible for the plantations to produce. It is evident, therefore, that some effort should be made to acquaint both the producer and the consumer with the other's difficulties and limitations.

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THE able presentation of these two papers requires no comment; however, there are points brought out that should be further emphasized. Considerable stress was laid on rate of curing and aging of crude rubbers, and the two points are important; however, thanks to the able research work and results obtained by the research men on modern accelerators and antioxidants, these two points are somewhat relegated to the background.

Every modern rubber factory today is undoubtedly blending various shipments of crude rubber which further equalize the curing rates of various shipments of rubber. This blending makes a still more uniform rubber.

Crude rubber as a whole is quite free from deleterious materials which affect either the cure or aging properties. However, the writer has seen quite large shipments of smoked sheet that were soft and mushy, and upon analysis found to contain manganese in appreciable quantities. Naturally, such deleterious materials cannot be tolerated. The two most important points were not stressed sufficiently:

CLEANLINESS. This means freedom from sand, bark, dirt, etc., contained in every type of crude rubber, particularly off-grades. Too much emphasis cannot be placed on the point that crude rubber should be freed on the plantations from these injurious and unwanted materials.

PLASTICITY OF CRUDE RUBBER. Very little has been done either by the producers or the consumers to obtain crude rubber of uniform plasticity. This point is of utmost importance, and methods, procedures, and equipment should be worked on by the committee suggested by Rhodes in preference to obtaining a formula or methods for uniform rate of cure and aging properties.

Every consumer of crude rubber is hampered appreciably by dirty rubber and nonuniform-plasticity rubber, and every effort should be made to correct these deficiencies.

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The paper by Sackett and the comments by Rhodes, Gray, and Nelson were presented before the Division of Rubber Chemistry at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935.

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Determination of Total and Free Selenium in Vulcanizates

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THE use of selenium as a vulcanizing agent in rubber stocks has increased considerably during the last few years. Only a small portion of the selenium combines with rubber, whereas the greater part remains free. When analyzing compounds containing selenium, it is interesting to determine selenium in both states. In spite of the available literature, there exist few specific methods of analyzing rubber containing selenium and no method of determining free selenium. The purpose of this paper is to give a method of determining free and total selenium in rubber compounds.

Determination of Total Selenium

Most methods of determining selenium involve treatment of the compound with oxidizing agents, such as hydrogen peroxide, nitric acid, or a mixture of hydrochloric and nitric acids. The selenious acid obtained is reduced to metallic selenium which may be determined by gravimetric, volumetric, or colorimetric methods.

The work of Blake (*2*) and of Shaw and Reid (*4*) outlines methods of determining selenium in rubber. The first involves oxidizing the rubber according to Carius and determining the selenium by iodometric titration. In the second method the rubber is oxidized by fusion with a mixture of sugar, potassium nitrate, and sodium peroxide.

In unpublished work, E. N. Korsunskaya has determined selenium in rubber compounds by oxidizing with nitric acid and reducing the selenious acid with hydrazine sulfate. The latter method seemed to be the simplest, and has been tested on a rubber stock of the following composition:

Formula of Rubber Stock No. 1

Smoked sheets	100
Zinc oxide	5
Stearic acid	1.5
Captax	0.7
Selenium	3
Sulfur	0.5
	110.7

The determination was accomplished in the following manner:

Two grams of rubber, cut into small pieces, were placed in a 250-cc. Erlenmeyer flask connected to a reflux condenser by a ground joint. Nitric acid (specific gravity 1.4) was introduced in portions of 3 to 4 cc. The flask was heated carefully with a small flame until complete destruction of rubber took place. After cooling, the solution was diluted with water to 150 to 200 cc. The precipitate (nitrosites) formed during this operation was filtered and washed several times with hot water. The filtrate was neutralized with 10 per cent aqueous ammonia and acidified slightly with hydrochloric acid (according to Wagenmann and Triebel, *5*, precipitation with hydrazine sulfate is more satisfactory in dilute hydrochloric acid). The flask containing the solution was then connected with a reflux condenser and 75 to 100 cc. of saturated aqueous hydrazine sulfate were added. For complete precipitation a small excess must be used.

The mixture was carefully heated until the selenium was converted to the black modification. After standing overnight the residue was filtered on a glass Schott's filter and washed with hot water until free of chloride and sulfate, then with alcohol and ether, and afterwards dried at 75° to 80° C. to constant weight (15 to 20 minutes).

The results of the experiments are shown in Table I, experiment A.

As shown in Table I, the results of parallel determinations check. Experimentally, this method is very simple, but the use of the large amounts of hydrazine sulfate is expensive. Besides hydrazine sulfate, such reducing agents as tin chloride, sulfur dioxide, etc., may be used. In using these reducing agents, nitric acid must first be removed. The work of Barkovsky and Babalova (*1*) shows that no losses of selenium occur in evaporating nitric acid from such a solution The authors have checked this.

After the destruction of the rubber by nitric acid, the mixture was washed into a porcelain cup and evaporated on a water bath until nearly dry. The residue was diluted with 100 cc. of hot water. After being cooled, the solution was filtered and placed in a 500-cc. Erlenmeyer flask. Two hundred and fifty cubic centimeters of hydrochloric acid (specific gravity 1.19) were added, and to this solution crystalline sodium sulfite was introduced in small portions. After each addition the flask was closed by a watch glass. A small surplus of sodium sulfite was introduced when the solution began to turn red. The flask was connected to a reflux condenser, heated to 40° to 50° C., and allowed to stand overnight. Considerable sodium salts precipitate but owing to their ready solubility in water, the determination of selenium is not affected.

The solution was poured through a filter and hot water added to the precipitate of selenium and sodium salts to dissolve the latter. Further filtration, washing, and drying were performed in the regular way.

Table I, experiment B, shows the results obtained by this method.

TABLE I. DETERMINATION OF SELENIUM IN COMPOUND 1

Experiment	Method of Precipitation	Amount of Selenium Calculated	Amount of Selenium Found
		%	%
A	Reducing with hydrazine sulfate	..	2.66
		2.71	2.68
B	Reducing with sulfur dioxide	..	2.58
		..	2.62
		..	2.69

Determination of Free Selenium

In developing a method of determining free selenium, detailed studies of the solubility of selenium were made. The authors tested chloroform, ether, benzene, acetone, carbon bisulfide, and carbon tetrachloride, with negative results.

Selenium dissolves in aqueous potassium cyanide, sodium sulfide, and sodium sulfite, giving chemical compounds. Potassium cyanide gives potassium selenocyanide. Sodium sulfide forms a selenosulfide and sodium sulfite gives a compound of the hyposulfite type. Selenium can be separated easily in its elementary state from each of the above solutions.

Potassium cyanide was discarded because of its poisonous character.

Sodium sulfide solutions had a tendency to separate free sulfur, which necessitated the use of a long and involved procedure.

One hundred cubic centimeters of sodium sulfite solution dissolve 0.1 gram of selenium after refluxing for 2 hours. The filtered and cooled solution on acidification with hydrochloric acid precipitates selenium which may be separated and weighed. In treating rubber in this manner free sulfur is also extracted, which precipitates with the selenium on acidification with hydrochloric acid. The authors have tested with success the possibility of using formalin for the selective precipitation of selenium. The use of sodium sulfite and formalin permits simultaneous determination of free selenium and free sulfur, the latter by the method of Bolotnikof and Gurova (*3*), which consists of iodometric titration of the hyposulfite formed.

This method has been tested on three mixtures of commercial selenium and sulfur, with the results shown in Table II.

TABLE II. DETERMINATION OF SELENIUM AND SULFUR IN MIXTURES

Selenium Taken	Selenium Found		Sulfur Taken	Sulfur Found	
Gram	*Gram*	%	*Gram*	*Gram*	%
0.1514	0.1492	98.5	0.0648	0.0605	93.4
0.1442	0.1431	98.8	0.0201	0.0190	94.5
0.1700	0.1685	99.1	0.0190	0.0180	94.5

The method of determining free selenium by means of extracting it with sodium sulfite has been checked by the

authors on several rubber stocks, compounds 1, 2, and 3. The rubber was milled and cut into pieces 1 mm. square with scissors. Two different curves of No. 1 were used.

	Rubber Formulas	
	No. 2	No. 3
Smoked sheets	100	100
Zinc oxide	5	...
Synthetic rubber	...	100
Stearic acid	1	3
Captax	0.5	1.4
Selenium	3	6
Sulfur	2	1
	111.5	211.4

When using the authors' method of degradation, approximately 30 hours are required to extract free selenium from rubber, the greater part of the selenium being extracted during the first 12 hours.

For determining free selenium, about 1 gram of rubber was placed in a 500-cc. Erlenmeyer flask, 200 cc. of 10 per cent sodium sulfite solution were added, and the mixture was boiled under reflux for 30 hours. A second treatment of the rubber was made with a fresh portion of sulfite solution to insure complete extraction. After cooling, the solution was filtered and the rubber washed with hot water. The flask containing the filtrate was again connected with the condenser, 75 cc. of formalin were added, and the solution was boiled for about an hour. After settling, the selenium was filtered on a Schott's filter and rinsed with water. The filtrate was transferred to another flask and the free sulfur determined. The residue on the filter was washed with hydrochloric acid and hot water until free of chlorides, then with alcohol and ether, and dried to constant weight.

Table III gives a summary of the determination of free selenium in these rubber compounds.

TABLE III. DETERMINATION OF FREE SELENIUM IN RUBBER STOCKS

Rubber	Time of Cure	Selenium (Calculated)	Free Sulfur Found	Free Selenium Found	Combined Selenium by Difference
	Min.	%	%	%	%
1	15	2.71	..	2.38	0.33
		2.71	..	2.36	0.35
	40	2.71	..	2.17	0.54
		2.71	..	2.15	0.56
2	..	2.69	0.15	2.29	0.40
			0.16	2.30	0.39
3	..	2.84	0.15	2.27	0.57
			0.18	2.15	0.69

Conclusions

The total selenium in rubber compounds may be determined by disintegrating with nitric acid and then separating the selenium by reducing the nitric acid solution with hydrazine sulfate, or by reducing with sulfurous acid after evaporation of the nitric acid. Free selenium is determined by extracting the rubber with aqueous sodium sulfite, from which selenium is precipitated by formalin.

Free sulfur is determined volumetrically by iodometric titration after precipitating selenium from sulfite solution.

Literature Cited

(1) Barkovsky, A. A., and Babalova, A. A., J. Plant Laboratory (U. S. S. R.), **4**, 306 (1934).
(2) Blake, J. T., IND. ENG. CHEM., **22**, 737, 740, 744, 748 (1930).
(3) Bolotnikof, V., and Gurova, V., *J. Rubber Ind.* (U. S. S. R.), **10**, 61–2 (1933).
(4) Shaw, E. H., Jr., and Reid, E. E., *J. Am. Chem. Soc.*, **49**, 2330 (1927).
(5) Wagenmann and Triebel, *Chem. Zentr.*, II, 273 (1930).

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Determination of True Free Sulfur in Vulcanized Rubber

A Modification of the Thiocyanate Method

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IT IS WELL known that the acetone extract of vulcanized rubber contains not only free sulfur, but in some cases also certain sulfur compounds which can be converted into sulfate by oxidation. Davis and Foucar (*2*) proposed a method to determine the true free sulfur contained in acetone extract of vulcanized rubber, as follows:

> The sample of the rubber stock is extracted by acetone as usual, the acetone is driven off from the extract, and the dried mass is heated under a reflux condenser with alcohol and a small lump of potassium cyanide. The free sulfur contained in the extract is converted into potassium thiocyanate. The solid cyanide remaining is removed, and alcohol is driven off by evaporation. The residue is treated with water, and a slight excess of nitric acid and some iron alum are added. The characteristic blood-red coloration of ferric thiocyanate appears. Titration is then carried out with a standard solution of silver nitrate until the red color disappears.

In applying this method, however, difficulty was always found in that some of the potassium cyanide used for the conversion of free sulfur into the form of thiocyanate goes into solution, rendering the end point of the final titration indistinct. To eliminate this difficulty, a modification was proposed by Castiglioni (*1*), consisting of shaking the mixture of cyanide and thiocyanate with a 20 per cent solution of formaldehyde to convert the cyanide into glycolic acid and hexamethylene tetramine, neither of which is considered to have any influence upon the final titration.

The present authors, however, found that there was much left to be desired in Castiglioni's method, because sufficient cyanide always remained unreacted to render the end point of the titration indistinct, and they were led to the idea that it is better to eliminate the cyanide completely by the use of a suitable solvent. Acetone was found eminently suitable

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for this purpose. It does not dissolve potassium cyanide to any appreciable extent, but at 22° C. dissolves 17.2 per cent of its weight of potassium thiocyanate (*3*).

To determine the suitability of acetone for this purpose, the following preliminary experiments were carried out:

1. Test for the insolubility of potassium cyanide in acetone.
2. Test for the limit of amount of cyanide influencing the end point of the titration of thiocyanate by silver nitrate solution.
3. Test for the separation of cyanide from thiocyanate by means of acetone.

Preliminary Experiments

TEST FOR THE INSOLUBILITY OF CYANIDE IN ACETONE. Various quantities of an alcoholic solution containing 0.00048 gram of potassium cyanide per cc. were accurately measured into flasks. The alcohol was distilled off and each residue digested with 20 cc. of acetone by gentle warming on the water bath under the reflux condenser for 30 minutes. After complete cooling, the acetone was filtered through a filter paper as quickly as possible and the filter washed several times with cold acetone. The cyanide on the filter and that adhering to the inside wall of the flask were dissolved with water, the solutions united, and then titrated with 0.01 *N* silver nitrate, with a few drops of 10 per cent solution of potassium iodide as indicator.

For comparison, the experiments were also carried out with the original alcoholic solution of cyanide without digestion with acetone. The results are shown in Table I.

TABLE I. ANALYSIS OF POTASSIUM CYANIDE BEFORE AND AFTER DIGESTION WITH ACETONE

No.	KCN Alcoholic Solution Taken	KCN in Alcoholic Solution Taken	0.01*N* $AgNO_3$ Solution Used	KCN Found
	Cc.	*Gram*	*Cc.*	*Gram*
1 Digested with acetone	5.0	0.0024	3.6	0.0023
2 Digested with acetone	10.0	0.0048	7.1	0.0046
3 Digested with acetone	20.0	0.0096	14.1	0.0091
4 Not digested with acetone	10.0	0.0048	7.3	0.0047
5 Not digested with acetone	20.0	0.0096	14.6	0.0094

The differences between the results for samples 2 and 3 which were digested with acetone and 4 and 5 which were not, are so slight that they may be regarded as within the limit of experimental error.

TEST FOR THE LIMIT OF AMOUNT OF CYANIDE INFLUENCING THE END POINT OF THE TITRATION OF THIOCYANATE WITH THE SOLUTION OF SILVER NITRATE. Several 5-cc. portions of a 0.107 *N* aqueous solution of purified potassium thiocyanate were accurately measured into conical flasks, to which various amounts of a 0.1016 *N* aqueous solution of potassium cyanide were added. The contents of the flasks were diluted with water up to about 25 cc. and acidified with a few cubic centimeters of 30 per cent nitric acid. Titration was carried out with a 0.05 *N* solution of silver nitrate, using a 5 per cent solution of ferric nitrate as indicator. The results are shown in Table II.

The results in Table II show that no influence appeared until the content of cyanide reaches to the amount of experi-

ment No. 6 or about 0.0005 mole of potassium cyanide in about 35 cc. of solution at the end of the final titration. Indistinctness of the end point was always observed when the concentration of cyanide exceeded this limit, increasing as the concentration of cyanide increased.

TABLE II. INFLUENCE OF POTASSIUM CYANIDE UPON THE TITRATION OF POTASSIUM THIOCYANATE WITH SILVER NITRATE SOLUTION

No.	0.107*N* KCNS Solution Taken	0.1016*N* KCN Solution Added	KCN in Solution Added	0.05*N* $AgNO_3$ Solution Used	End Point
	Cc.	*Cc.*	*Gram*	*Cc.*	
1	5.0	0	0	10.7	Distinct
2	5.0	1.0	0.0066	10.6	Distinct
3	5.0	2.0	0.0132	10.6	Distinct
4	5.0	3.0	0.0198	10.6	Distinct
5	5.0	4.0	0.0264	10.5	Distinct
6	5.0	5.0	0.0330	10.8	Somewhat indistinct
7	5.0	10.0	0.0660	10.8	Somewhat indistinct
8	5.0	15.0	0.0990	10.8	Somewhat indistinct

TABLE III. TITRATING THIOCYANATE WITH SILVER NITRATE AFTER SEPARATING CYANIDE BY MEANS OF ACETONE

No.	0.0996*N* KCNS Alcoholic Solution Taken	Solid KCN Added	0.05*N* $AgNO_3$ Solution Used	End Point
	Cc.	*Gram*	*Cc.*	
1	10.0	0	19.9	Distinct
2	10.0	About 1	19.8	Distinct
3	10.0	About 1	19.9	Distinct

TABLE IV. COMPARISON, THROUGH ESTIMATION OF PURE SULFUR, OF RESULTS OBTAINED BY MODIFIED AND OXIDATION METHODS

Method Used	Sample of Sulfur Taken	Time of Boiling with KCN	$BaSO_4$ Found	Sulfur Found
	Gram	*Min.*	*Gram*	%
New modified method	0.0100	30	....	99.4
	0.0100	40	....	99.4
	0.0100	60	....	99.4
Oxidation method	0.0100	..	0.0727	99.9
	0.0158	..	0.1149	99.9

TEST FOR THE SEPARATION OF CYANIDE FROM THIOCYANATE BY MEANS OF ACETONE. Ten cubic centimeters of a 0.0996 *N* alcoholic solution of purified potassium thiocyanate were accurately measured into a 100-cc. flask and diluted with alcohol up to about 50 cc. To this solution was added about 1 gram of potassium cyanide and the flask was heated under a reflux condenser for half an hour. The solution was evaporated to dryness, 30 cc. of acetone were added to the residue and the flask was shaken for a few minutes, while being gently warmed. On cooling, the contents of the flask were quickly filtered and washed several times with acetone. The filtrate was received in a 300-cc. flask and the acetone distilled off. The residue in the flask was dissolved in water, and 5 cc. of 30 per cent nitric acid were added. Titration was carried out with 0.05 *N* solution of silver nitrate, with 5 per cent solution of ferric nitrate as indicator. The results are shown in Table III.

These results show that acetone is a suitable solvent for removing cyanide and giving a distinct end point to the titration of thiocyanate with the solution of silver nitrate. From this fact, the method proposed by Davis and Foucar may be successfully modified and the difficulty of indistinct end point eliminated.

Procedure of Modified Method

Heat the dried acetone extract of vulcanized rubber for half an hour with 25 cc. of absolute alcohol and a small lump of potassium cyanide under a reflux condenser on a water bath, distill off the solvent, shake the dried mass with about 30 cc. of acetone for a few minutes, remove the undissolved residue by filtration, and wash with acetone. After evaporating the filtrate on the water bath, dissolve the dried substance with 50 cc. of water, add 5 cc. of 30 per cent nitric acid and a few drops of 5 per cent solution of ferric nitrate; shake the solution vigorously, and titrate with 0.1 *N* solution of silver nitrate until the blood-red coloration of ferric thiocyanate has disappeared.

Calculate the free sulfur content in original rubber sample as follows:

$$\text{Percentage of free sulfur} = \frac{0.003206 \times \text{cc. of } 0.1\,N\ AgNO_3 \text{ solution used for titration}}{\text{weight of sample (grams)}} \times 100$$

Application of Modified Method

Analysis of Pure Sulfur. To test the accuracy of the modified method, it was applied to the estimation of sulfur purified by means of sublimation in a glass retort, the purified sulfur being monoclinic crystal with a melting point of 119.0°–119.2° C. and leaving no trace of ash when incinerated. The results were also compared with those obtained by the ordinary oxidation method whereby the sample is oxidized into sulfate by means of bromine and fuming nitric acid. The results obtained by the two methods are almost concordant with each other, as shown in Table IV.

Analysis of Rubber Stocks. For exemplifying the application of the modified method, the rubber compounds given in Table V were prepared, and the ordinary oxidation method was also applied to the same samples for comparison. The results are shown in Table VI.

Table VI indicates that samples 1 and 3 give the same results by both methods within the limit of experimental error; on the other hand, sample 2 gives somewhat higher results by the oxidation method than by the modified method. This is probably due to the fact that the acetone extract of sample 2 contains an undervulcanized portion of the incorporated brown substitute containing some combined sulfur which can be oxidized to sulfate.

Applications were also made for the analysis of rubber insulation of a flexible joint wire manufactured by a Japanese cable maker, and a stamp mat employed in the post office. The results are shown in Table VII.

For the rubber insulation, the results of both methods are very close. For the stamp mat, however, the difference in results is rather remarkable.

Summary

The limit of quantity of potassium cyanide was determined as regards the interference with the end point of the titration of potassium thiocyanate with silver nitrate solution.

Acetone was found to be a suitable solvent for the separation of potassium cyanide from potassium thiocyanate.

TABLE V. COMPOSITION OF RUBBER STOCKS FOR ANALYSIS

No.	Composition					Vulcanization	
	Standard smoked sheet	Zinc oxide	Sulfur	D. P. G.	Brown substitute	Steam pressure *Kg./sq. cm.*	Time *Min.*
1	100	5	5	1	0	2.81	30
2	100	5	5	1	5	2.81	30
3	100	5	40	1	0	4.22	300

TABLE VI. RESULTS OF ANALYSIS OF PREPARED RUBBER STOCKS

No.	Free Sulfur Found	
	New modified method	Oxidation method
	%	%
1	2.66	2.76
	2.66	2.77
2	1.17	1.30
	1.17	1.31
3	0.21	0.27
	0.21	0.28

TABLE VII. ANALYSIS OF FREE SULFUR IN COMMERCIAL RUBBER GOODS

Kind of Sample	Free Sulfur Found	
	New modified method	Oxidation method
	%	%
Rubber insulation	0.13	0.17
	0.13	..
Rubber stamp mat	1.01	1.20
	1.01	1.20

A new modified method was proposed for the determination of true free sulfur in vulcanized rubber, by the use of acetone to remove the cyanide which renders obscure the end point of the titration of thiocyanate with silver nitrate solution. The proposed method was applied to the analysis of pure sulfur and some rubber goods, and was ascertained to be accurate and easy to carry out, requiring no special apparatus.

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Literature Cited

(1) Castiglioni, A., *Z. anal. Chem.*, **91**, 32 (1932); *Rubber Chem. Tech.*, **6**, 412 (1933).
(2) Davis, C., and Foucar, L. J., *J. Soc. Chem. Ind.*, **31**, 100 (1912); W. A. Caspari, "India-Rubber Laboratory Practice," p. 116, London, Macmillan Co., 1914.
(3) Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Auflage 5, Bd. 1, S. 729, Berlin, Julius Springer, 1923.

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A Fatigue Cracking Test for Tire Tread Compounds

Some of the Laws of Fatigue

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AN IMPORTANT factor in the service rendered by a tire tread is its ability to resist cracking. Cracking of tire treads in service may be classified into two kinds or phases—the initiation or start of cracks, and the growth of cracks or cuts once started—and the two phases must be differentiated. Nearly all tires in service soon develop small cracks or "checking" due to the action of ozone in the atmosphere (*9*), and may suffer cuts due to sharp objects on the road. In many cases such cuts and ozone cracks may be harmless, but if the cracks grow too rapidly they will extend to the carcass before the tire is worn out (*4*). We define the growth of cracks under the influence of mechanical action as fatigue cracking.

The quality of rubber in respect to its resistance to fatigue cracking can be improved by addition of antioxidants (*3*, *7*), and by such factors as the proper choice of accelerators (*4*), the proper balance of fillers (*1*, *3*), and the proper cure. The quantitative evaluation of such chemicals and compounding ingredients in the laboratory depends upon the validity and precision of a test. It is the purpose of this paper to describe a laboratory test which has been found to correlate with shoulder cracking in tires, and to present data from which certain laws of fatigue cracking have been deduced.

In general, a laboratory test to be valid for the prediction of service should give results in agreement with those obtained in service, and should be reproducible. A laboratory fatigue cracking test for tire tread stocks should simulate service by measuring the rate of growth of cracks after their initiation (*4*), should operate between constant strain limits rather than constant stress limits (*3*), and should be capable of operation within the range of strains actually encountered in tires. The cracks should occur in a definite region on the test piece, and the mechanism of their growth should be of the same nature as in tires. The ratings should be quantitative. For the laboratory study of tread compounds the test specimens should be easily, accurately, and cheaply prepared.

A large number of samples must be tested simultaneously. The test should be fairly rapid.

A number of laboratory cracking tests have been described in the literature, but none meets all the above-mentioned conditions.

The test herein described consists of starting cracks in a grooved, molded test specimen by means of ozone; causing the cracks to grow by bending the test specimen through repeated cycles of strain with a suitable machine; and estimating the degree of cracking from the loss of bending moment as measured in a suitable apparatus. The test meets most of the conditions outlined above. The cracks are produced in much the same way as in service, and the cracked specimens have the same appearance as do cracked tires. The method of rating the cracking is independent of any judgment on the part of the operator, and the test does not require close attention.

The chief disadvantage of the test is that it is slow compared with some other laboratory tests (*1*, *8*), for the flexing machine cannot be operated at the very high speeds of which some other machines are capable. When the tests are run at low strain limits they may last several weeks, but in such cases it is believed that what is lost in time is gained in validity. In certain cases, the time required for a test may be reduced by working to high strain limits or by running the test at elevated temperatures.

Description of Test

TEST SPECIMEN. A diagram of the molded test specimen is shown in Figure 1.

It consists entirely of tread rubber without any fabric backing. Its essential feature is the single U-shaped groove, running across the center. The groove has a half-round bottom of 0.1588-cm. (0.0625-inch) radius, with straight sides exactly tangent, and it extends half-way through the test piece. It is important that the mold rib which forms the groove should be accurately machined and polished.

The authors have found it convenient to mold the samples in slabs about 15.8 cm. (6.25 inches) long, from which six test specimens may be cut. The test specimens are usually cut 2.5 cm. (1 inch) wide, but the exact width is not important.

Strains may be induced in the test specimen by bending it so as to open or close the groove, and the maximum surface strain always occurs in the bottom of the groove. Figure 2 shows the relationship between the angle of bend and the surface strain in the bottom of the groove of an uncracked test specimen. By "angle of bend" is meant the angle of displacement from the straight, molded shape—that is, the difference between 180° and the dihedral angle formed by the back of the test specimen. Thus, an angle of bend of 60° means that the test specimen is bent to a dihedral angle of 120°. The surface strain data shown in Figure 2 were ob-

tained by placing short marks in the bottoms of the grooves of about 60 test specimens and measuring the lengths of the marks by means of a microscope, when the test specimens were

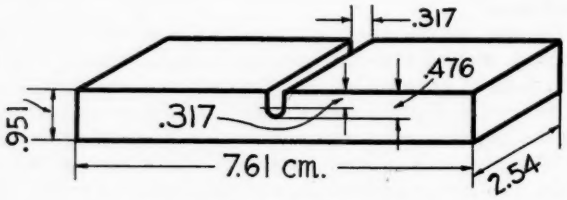

FIGURE 1. TEST SPECIMEN

bent to various angles in the flexing machine. It will be noted that there is a consider able variation in the measured surface strain at any given angle of bend. Some of this variation may be due to actual variations among the samples, but it is believed that most of the variation is due to errors in the measurements. The authors have observed no systematic variations in the relationship between angle of bend and surface strain for samples molded from stocks with widely differing moduli.

FLEXING MACHINE. The essential feature of the flexing machine is the mechanism pictured in Figure 3, which consists of hinged angle bars for holding the test pieces.

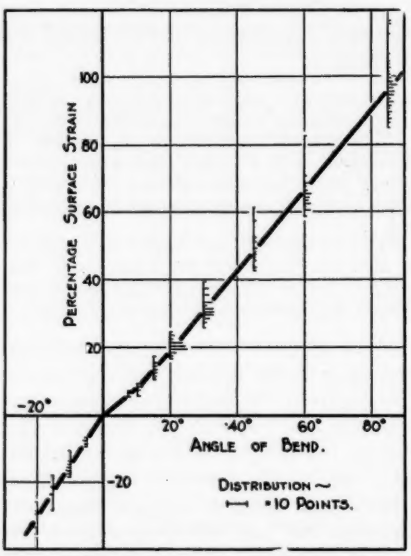

FIGURE 2. RELATIONSHIP BETWEEN ANGLE OF BEND AND SURFACE STRAIN IN UNCRACKED TEST SPECIMENS

The test pieces fit loosely into a slot in the lower or stationary bar, and are tightly clamped to the upper or movable bar, by means of metal strips held by thumb screws. The hinges are so constructed that their axis is collinear with the approximate center-of-bend of the test pieces—i. e., the axis is 0.238 cm. (0.094 inch) in front of the faces of the back bars and in line with the centers of the grooves in the test pieces. The edges of the bars are placed 1.27 cm. (0.5 inch) apart, so that the center sections of the test pieces are left free of clamping.

The position of the fixed bar is adjustable within an angle of about 90°. Through the adjustment of the throw of the crank, the movable bar may be vibrated through any angle within +45° and −45° from its central position. Thus the angle of bend to which the test pieces are to be submitted may be varied through large limits.

To develop fatigue cracking in the test pieces, the movable bar is vibrated by driving it with any suitable mechanism. One mechanism consists of a slide driven by an inverted

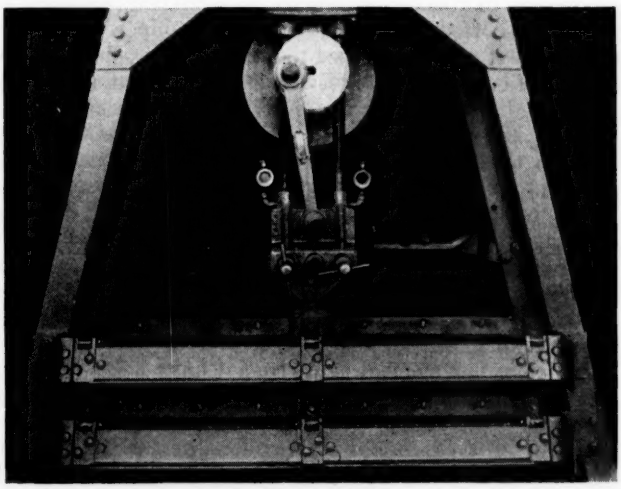

FIGURE 3. FLEXING MACHINE

DeMattia flexing machine, as shown in Figure 3. In another type of machine a simple system of levers driven by a cylindrical cam is used. The machines are usually run at the maximum speed at which they will run smoothly—i. e., 350 to 400 cycles per minute.

MEASUREMENT OF DEGREE OF CRACKING. The degree of cracking in a test piece at any time is determined by measuring its bending moment when it is bent to a definite dihedral angle—namely, 135°. Figure 4 shows the apparatus that is used.

It consists of a hinged clamp, one end of which is fastened to a board and the other end of which carries a pointer and is movable. The back side of the movable end is cut away so that the

test piece may slip slightly and adjust itself to its natural position. The hinge is below the test piece and so placed that its extended axis would pass through the center of that portion of the test piece just under the groove. When the sample is placed as shown in Figure 4, except that the axis is in the vertical position, the pointers are brought together, and the torque or bending moment to bend the sample to a dihedral angle of 135° is read from the elongation of the spring.

The degree of cracking—i. e., the average percentage depth of cracks—is assumed to be equal to the percentage loss of bending moment, based upon the bending moment of the uncracked sample after the preliminary flexing. This assumption appears to be justified for practical purposes from the following considerations. Figure 5 illustrates the relationship between the percentage loss of bending moment (as measured at 45° bend) and the percentage depth of smooth, straight, even cuts made with a razor blade. The solid curve represents the average experimental relationship, while the dotted line shows the relationship required for equality. It will be observed that, for the cuts, the percentage loss of bending moment is usually a little greater than the percentage depth of cut. However, fatigue cracks are usually irregular and of uneven depth. For a given loss of bending moment the deepest portions of the cracks (which count most in service) are undoubtedly deeper than the even cuts. Hence for cracked test pieces the percentage loss of bending moment is probably more nearly equal to the percentage depth of cracks than in the case of the cuts. In one case the depth of a crack was measured microscopically at two points and gave percentage depths of 35 and 42, respectively. The loss of bending moment was 39 per cent.

If the bending moment is to give a definite measure of the degree of cracking, it is necessary that the modulus of the rubber should not change appreciably between the determination of the initial bending moment and subsequent determinations of bending moment. It has been found that unflexed samples are always stiffer than samples which have been flexed. The uncracked samples suffer a loss of bending moment during the first few cycles of flexing without any visible cracking, but after from 5 to 100 kilocycles (depending upon the angle of bend) the bending moment becomes constant for tests at room temperature, and there is no further loss until cracks appear. The "initial bending moment" upon which the degree of cracking is based is always taken on samples which have had considerable flexing, and in which the bending moment has become constant.

Thus it appears that for tests run at room temperature the percentage loss of bending moment gives a direct measure of the average percentage depth of cracks.

The measurement of the bending moment at a dihedral angle of 135° is more or less arbitrary, and it is likely that any angle greater than 90° could be used, so long as the same

angle was used for all samples which are to be compared. The authors have chosen 135° merely because it is a convenient angle for their particular test specimen and gives reproducible values of the bending moment over a suitable range. Angles too near 180° should not be used, however, since there are small variations due to the way in which different samples fit into the clamps. At a dihedral angle of 135° such variations are of relatively small consequence, but at greater angles the relative effects would be greater.

Procedure for Testing

1. The samples are placed in the flexing machine and are flexed for 5 to 10 kilocycles if tested at a high angle of bend (85°) or for 50 to 200 kilocycles if tested at a low angle of bend (20° to 30°). This removes the stiffness from the samples and makes the bending moment reproducible.

2. The samples are removed from the flexing machine and their bending moments are measured to get the values for the uncracked samples, using the apparatus shown in Figure 4. The sample is placed in the apparatus with the groove out. The pointer is moved to an angle of about 75° and vibrated several times, then allowed to come back to about 30°, and again vibrated. Finally, the spring is stretched with one hand, while the pointer is vibrated with the other, until the pointer holds at 45°. The value of the bending moment is read from the scale.

3. It is usually well to repeat steps 1 and 2. This gives two readings of the bending moment on the uncracked samples. The average is taken as the zero load.

4. The samples are cracked in ozone as follows: They are placed in frames which hold them to a 20° bend, and are then put into an ozonized atmosphere until the entire surface of the groove is checked—covered with many very small cracks. These cracks should not be too deep, but just barely visible to the naked eye.

The samples are removed from the 20° frames and placed in

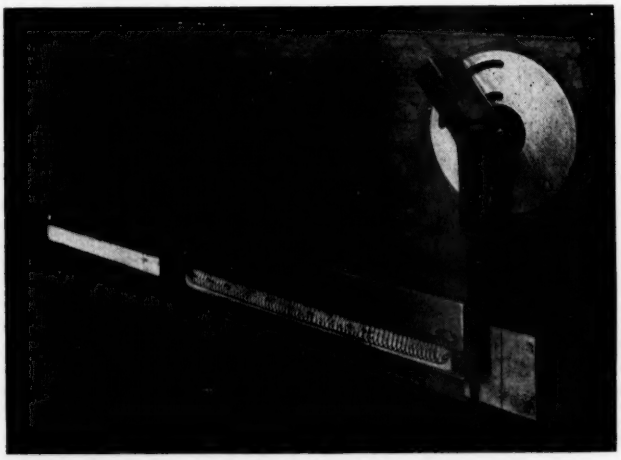

FIGURE 4. APPARATUS FOR MEASUREMENT OF BENDING MOMENT

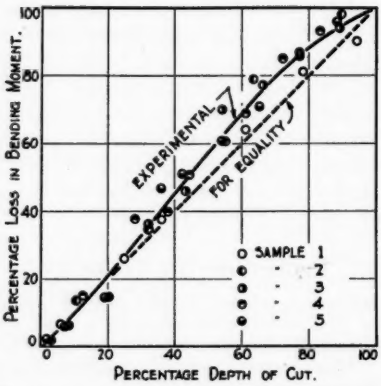

FIGURE 5. RELATIONSHIP BETWEEN PERCENTAGE LOSS OF BENDING MOMENT AND PERCENTAGE DEPTH OF CUTS OR CRACKS

frames which hold them to 7° bend. They are again put into the ozonized atmosphere until the ozone cracking is completed—that is, until the samples would show from 10 to 15 per cent loss in bending moment, which is the amount required to eliminate the induction period. (Figure 6.) A little experience will enable the operator to judge when the cracking is sufficient. When the ozone cracking has been properly done, the sample has a single broken line of ozone cracks all the way across the sample and in the bottom of the groove.

In the ozone cracking treatment the concentration of ozone is immaterial except as it determines the time necessary to get cracking. The authors prefer a low concentration, which is high enough so that the odor is very noticeable and considerably higher than atmospheric concentrations. The checking of the surface when the samples are at an angle of bend of 20° leads to a series of small cracks similar to those observed on tires in service. If this step is omitted the ozone cracks may be few and large and difficult to reproduce. For the final ozone cracking an angle of bend of about 7° must be used, so that only the bottom of the groove will suffer deep cracking. The exact amount of ozone cracking (within limits) is immaterial, since the effects of variations in the amount of ozone cracking are eliminated in the method of rating.

5. The bending moment is measured as described in step 2, from which the degree of ozone cracking may be calculated.

6. Fatigue cracking is induced in the samples by flexing them in the flexing machine. At intervals during the test the samples are removed from the machine, their bending moments are measured as in step 2, and the counter reading is recorded. The frequency at which data are taken depends upon the rate of cracking, and must be judged by the operator upon the basis of experience. In general, the intervals should be such as will give 5 to 10 per cent loss in the bending moment. For high-angle tests data should be taken about every 150 kilocycles. For low-angle tests the intervals might be 500 to 3000 kilocycles.

Rating the Samples

BY RATE OF GROWTH OF CRACKS. It has been found experimentally that, for most stocks and most flexing cycles,

the rate of growth of cracks, as measured by the rate of loss of bending moment in terms of cycles of flexing, is constant up to about 60 per cent loss of bending moment. Hence the authors prefer to rate the samples in terms of $\Delta Kc/\Delta$ per cent—i. e., the number of kilocycles of flexing required to produce 1 per cent deterioration in the sample. The $\Delta Kc/\Delta$ per cent values may be calculated as follows: For each sample the bending moment data are calculated to percentage deterioration—i. e., percentage loss of bending moment, based upon the zero load values. The percentage deterioration is plotted against the total number of kilocycles of flexing, using cartesian coördinate paper. The best straight line is drawn graphically through the plots and its slope is taken as the $\Delta Kc/\Delta$ per cent value. In drawing the straight lines, points below 10 and above 60 per cent deterioration should in general be neglected.

In Terms of a Definite End Point. In some cases it may be desirable to rate the samples in terms of a definite end point, such as 50 per cent fatigue cracking. The percentage deterioration values are calculated as directed above. From these values, the values for ozone cracking are subtracted in each case to give the percentage fatigue cracking. The number of kilocycles of flexing for 50 per cent (or any other degree) of fatigue cracking may be estimated by interpolation.

Characteristics of Test

Induction Period. When an uncracked specimen is flexed in air there is a period during which there is no loss of bending moment and no visible cracking. This may be termed an induction period. Following the induction period, cracks appear and grow at a steady rate. Curve 1 of Figure 6 shows typical data on a sample which was not subjected to ozone cracking. This curve represents a flexing test in which the strain cycle was $-5°$ minimum bend to $+60°$ maximum angle of bend. When the maximum bend is higher, say 90°, the induction period is shorter, both absolutely and relative to the life of the sample.

In other flexing tests which have been described (*1*, *6*, *7*, *8*) the induction period occurs, and in general the ratings of these tests include both the induction period and the rate of growth of cracks after they form.

Elimination of Induction Period by Ozone. If the cracks are initiated by the action of ozone, the induction period is eliminated, as is illustrated by curves 2, 3, and 4 of Figure 6. It is believed that for tires in service the cracks are usually initiated by the action of ozone. Often small ozone cracks may be observed on tires which have been in service only a few hours. It is partly for this reason that the authors start the cracks with ozone in their test. Initiation of cracks with ozone shortens the time of the test. Gray, Karch, and Hull (*4*) obtain a similar result with cuts.

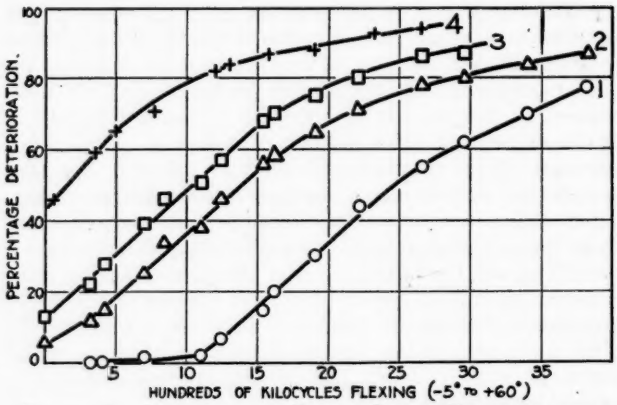

FIGURE 6. ADDITIVITY OF STATIC OZONE CRACKING AND FATIGUE CRACKING

ADDITIVITY OF STATIC OZONE CRACKING AND FATIGUE CRACKING. The effects of static ozone cracking and of fatigue cracking appear to be additive. (Figure 6.) If curves 2, 3, and 4, which represent samples in which the cracks were

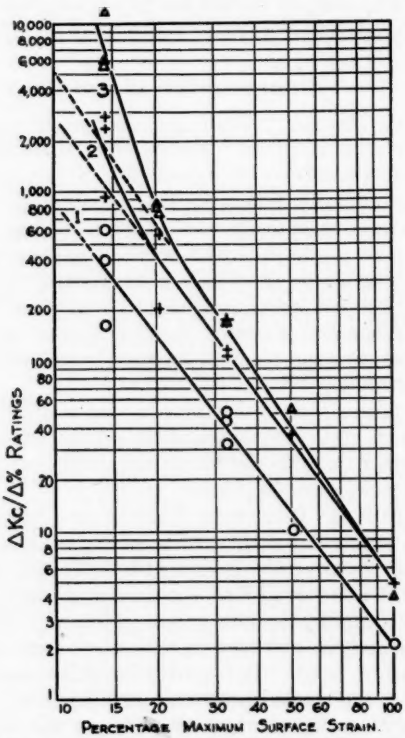

FIGURE 7. EFFECT OF MAXIMUM STRAIN

started with ozone, were moved along the X-axis they could all be made to coincide with curve 1, representing a sample which had no ozone cracking. This shows that cracks produced by ozone are the same in their effect as cracks produced by flexing only. Within limits, the amount of ozone cracking has no effect upon the subsequent rate of fatigue cracking.

RATE OF GROWTH OF CRACKS VS. DEGREE OF CRACKING. When the minimum strain in the flexing cycle is nearly zero, the rate of growth of cracks is nearly constant and is independent of the degree of cracking, up to about 60 per cent deterioration. This is illustrated by curves 2, 3, and 4 of Figure 6 and by curves 1 and 2 of Figure 8, which are approximately straight lines within the range 15 to 60 per cent deterioration. Beyond about 60 per cent deterioration the rate of cracking decreases and tends to approach 100 per cent deterioration asymptotically. In practice, points beyond 60 per cent deterioration are usually neglected.

When the minimum strain in the flexing cycle is positive—i. e., the sample is not brought back to zero bend—the rate of cracking may not be constant during the entire life of the sample. Curves 3 and 4 of Figure 8 illustrate the progress of cracking when the angle of strain is +20° minimum to +40° maximum angle of bend.

When stocks are to be rated for their resistance to shoulder cracking in tires, the authors usually use an angle of bend of zero to a maximum. Hence for most tests the rate of growth of cracks is constant and independent of the degree of cracking, and the method of rating the samples by rate of growth of cracks applies.

Effects of Variables in Testing Conditions

EFFECT OF MAXIMUM STRAIN. When samples are cracked by flexing them between the limits zero and a maximum value of surface strain, the rate of growth of cracks is very sensitive to the value of the maximum strain. For a considerable range of maximum strain values, the following relationship holds approximately:

$$R = k/S^n$$

where R is the number of kilocycles of flexing required to cause 1 per cent deterioration in the test specimen—$\Delta Kc/\Delta$ per cent—S is the percentage maximum surface strain as measured on the uncracked specimens, while k and n are constants for any particular stock and cure.

If the values of R and S are plotted on logarithmic scales, straight-line curves are obtained, as is illustrated by the curves of Figure 7, which are straight lines from 100 per cent maximum surface strain to about 20 per cent maximum surface strain. The values of n are given by the slopes. For most stocks, n has a value of approximately +3.

The qualitative dependence of the rate of cracking upon the value of the maximum strain has been reported by other workers (*3*, *7*), but no quantitative generalizations appear to have been attempted.

EFFECT OF MINIMUM STRAIN. When samples are cracked by flexing them between the limits of a positive minimum and a given maximum strain, the rate of growth of cracks is slower the greater the value of the minimum. This is illustrated by the curves of Figure 8. Curves 1 and 2 represent samples flexed from 0° to 40° bend, while curves 3 and 4 represent samples of the same stock flexed from +20° to +40° bend. With the latter cycle the rate of growth of cracks was only about one-fifth of that obtained with the former cycle.

A similar effect has been observed by Busse (*2*) in regard to tear resistance.

It is recognized that surface strains as measured on uncracked test specimens are lower than the actual strains in the bottom of the cracks (*2*), but for cracks of any given depth and sharpness the actual strains in the cracks are probably proportional to the over-all strain in the specimen—i. e., to the measured surface strains. The true endurance limits of strain for rubber compounds would therefore be higher than those calculated, but should be proportional to the calculated values. For purposes of tire design we are limited to the over-all strains instead of the actual strains in the cracks; hence the authors measured the strains in test specimens as over-all strains in order to facilitate correlation with tires.

The knowledge of "safe limits" for tread stocks has been useful in controlling shoulder cracking in tires.

Busse (*2*) has observed a kind of endurance limit in connection with tears started from cuts. He flexed cut samples to constant maximum over-all strains, varying the minimum strains, and found that as the minimum was increased the lives of the samples became infinite. In the author's tests, however, the cracks never branch into arrowheads and grow backwards, as Busse observed with the cuts.

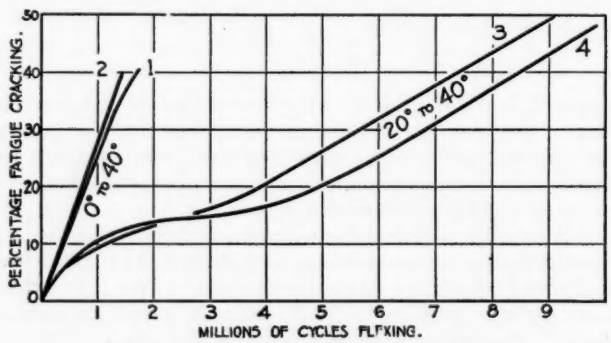

FIGURE 8. EFFECT OF MINIMUM STRAIN

ENDURANCE LIMITS. Curves 3 and 4 as plotted in Figure 7 are similar in shape to the *S-N* curves which are plotted in the fatigue testing of metals (*5*). At low values of maximum strain, the curves depart from the straight-line relationship and tend to become parallel with the log ($\Delta Kc/\Delta$ per cent) axis. This indicates that an "endurance limit" is being approached at which the rate of growth of cracks would be indefinitely slow.

In the authors' experiments no true endurance limit was reached, for in no case was the strain so low that no cracking at all took place, but for practical purposes "safe limits" were reached in many cases. It has been calculated that for shoulder cracking in passenger size tires a rate of crack growth corresponding to a $\Delta Kc/\Delta$ per cent value of about 3500 is safe for the life of a tire, allowing a safety factor of 5 in the rate of crack growth. The values of maximum surface strain corresponding to this safe rate of cracking may be read from curves of the type shown in Figure 7. Curve 1 represents a stock which contained no antioxidant. In this case the safe limit was not reached in the laboratory tests, but by extrapolating the curve as a straight line we would arrive at a value of about 6 per cent surface stretch. Curve 2 represents the same stock with 0.5 part BLE added. (BLE is a commercial antioxidant which is a diarylamine-ketone reaction product.) The estimated safe limit is about 12 per cent. Curve 3 represents the same stock with 1.0 part BLE added. The estimated safe limit is about 16 per cent.

EFFECT OF SPEED OF TESTING. The rate of cracking is measurable in terms of cycles of flexing, and when so measured is independent of the speed of the machine. This is in agreement with the observations of other workers (*7*). Also, no effects of short rest periods have been observed.

EFFECT OF TEMPERATURE. Increasing the temperature of the air surrounding the samples always increases the rate of cracking in the authors' test. This is contrary to the observations of Somerville (*7*) who found that the rate of cracking decreased with increased temperature. His test pieces took on considerable permanent set at elevated temperatures, while the authors believe their test pieces to be fairly free from permanent set even at elevated temperatures, although other effects must sometimes be taken into consideration.

For rating shoulder cracking in tires the authors always test stocks at room temperature, about 25° C.

Effects of Variables in Stocks

ANTIOXIDANTS. In agreement with other workers, the authors find that the addition of antioxidants decreases the rate of cracking. This is illustrated by the curves of Figure 6. Curve 1 is for a tread stock without antioxidant, while curves 2 and 3 are for the same stock with 0.5 and 1.0 part

of BLE added. The relative effect of the antioxidant is greater at the low angle tests than at the high angle tests. The addition of antioxidant raises the endurance limit.

CURE. In tests on unaged samples at room temperature no general law for effect of cure has been observed with the authors' test. For any given stock, differences in rates of cracking among different cures are usually observed; with some stocks the undercures crack the faster, while with others the overcures crack the faster. In tests on aged samples, the overcures usually tend to crack the faster, although exceptions have been observed.

Other workers (*1*, *4*, *7*) have found that overcures crack worse than undercures.

AGING. Samples which have been shelf-aged, aged in the Geer oven, or aged in the oxygen bomb, almost invariably crack faster than the unaged samples. Other workers (*4*) have found that oven aging of tires causes them to crack more rapidly.

Precision of Test

The relative deviation from the mean of duplicate samples depends somewhat upon the angle of bend used in the test. Long-time tests run at low angles of bend are usually less reproducible than short-time tests run at a high angle of bend. In one test run at 0° to 60° bend, wherein 3 groups of 6 duplicate samples were tested, the percentage probable errors of the means were 4.48, 4.38, and 3.86 per cent, respectively. In another series of tests run at 0° to 30° and 0° to 20° bend, the average percentage probable error of the means of groups of 8 or 9 duplicates was about 25 per cent.

According to the theory of probability, it may be shown that if the difference between two quantities which are to be compared is 1.4 times the probable error of each quantity, there will be about 9 chances out of 10 that the difference is real. It follows that, if the test is capable of giving ratings for stocks with a probable error of 4.3 per cent it is capable of detecting differences in stocks of the order of 6 per cent. If the probable error of the ratings is 25 per cent, it can detect differences only of the order of 35 per cent. Differences in the rates of cracking of tread stocks as great as 500 per cent have been observed, while differences of the order of 60 per cent are not uncommon.

The variations observed with this test are not all due to errors in the cracking test itself, but may be due in large part to actual variations in the samples tested, caused by uncontrolled variables in mixing, molding, and curing.

Fatigue cracking tests are, in general, among the least reproducible of the physical tests on rubber. In order to get reliable results it is necessary to test many duplicate samples. The authors recommend testing at least 6 duplicates, and preferably more.

Correlation with Service

Analyses of data from the test have shown good correlation with tire cracking in service. Compounds which have shown up well in the laboratory test have shown less tendency to crack in tires. The test has been useful in the evaluation of such factors as antioxidants, accelerators, and softeners for their effects upon the resistance to cracking of tread stocks.

In certain cases where correlation tests have been made, the laboratory test has shown good quantitative agreement with shoulder cracking in tires. From laboratory data, together with a knowledge of the strains suffered by tire treads in service, the authors have been able to predict with fair accuracy the mileages at which troublesome shoulder cracking is likely to occur.

Literature Cited

(1) Booth, E. W., *India Rubber World*, **82**, No. 6, 53–5 (1930).
(2) Busse, W. F., IND. ENG. CHEM., **26**, 1194–9 (1934).
(3) Cooper, L. V., *Ibid.*, Anal. Ed., **2**, 391 (1930).
(4) Gray, H., Karch, H. S., and Hull, B. F., *Ibid.*, **6**, 265–8 (1934).
(5) Moore, H. T., and Kommers, J. B., "The Fatigue of Metals," 1st ed., pp. 122–4, New York, McGraw-Hill Book Co., 1927.
(6) Neal, A. M., and Northam, A. J., IND. ENG. CHEM., **23**, 1449 (1931).
(7) Somerville, A. A., *Inst. Rubber Ind. Trans.*, **6**, 130–70 (1930).
(8) Torrence, P. M., and Peterson, L. C., *India Rubber World*, **80**, No. 4, 62 (1929); *Rubber Chem. Tech.*, **2**, 525–7 (1929).
(9) Van Rossem, A., and Talen, H. W., *Kautschuk*, **7**, 79–86, 115–17 (1931); *Rubber Chem. Tech.*, **4**, 490–504 (1931).